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NATO/CCMS Pilot Study

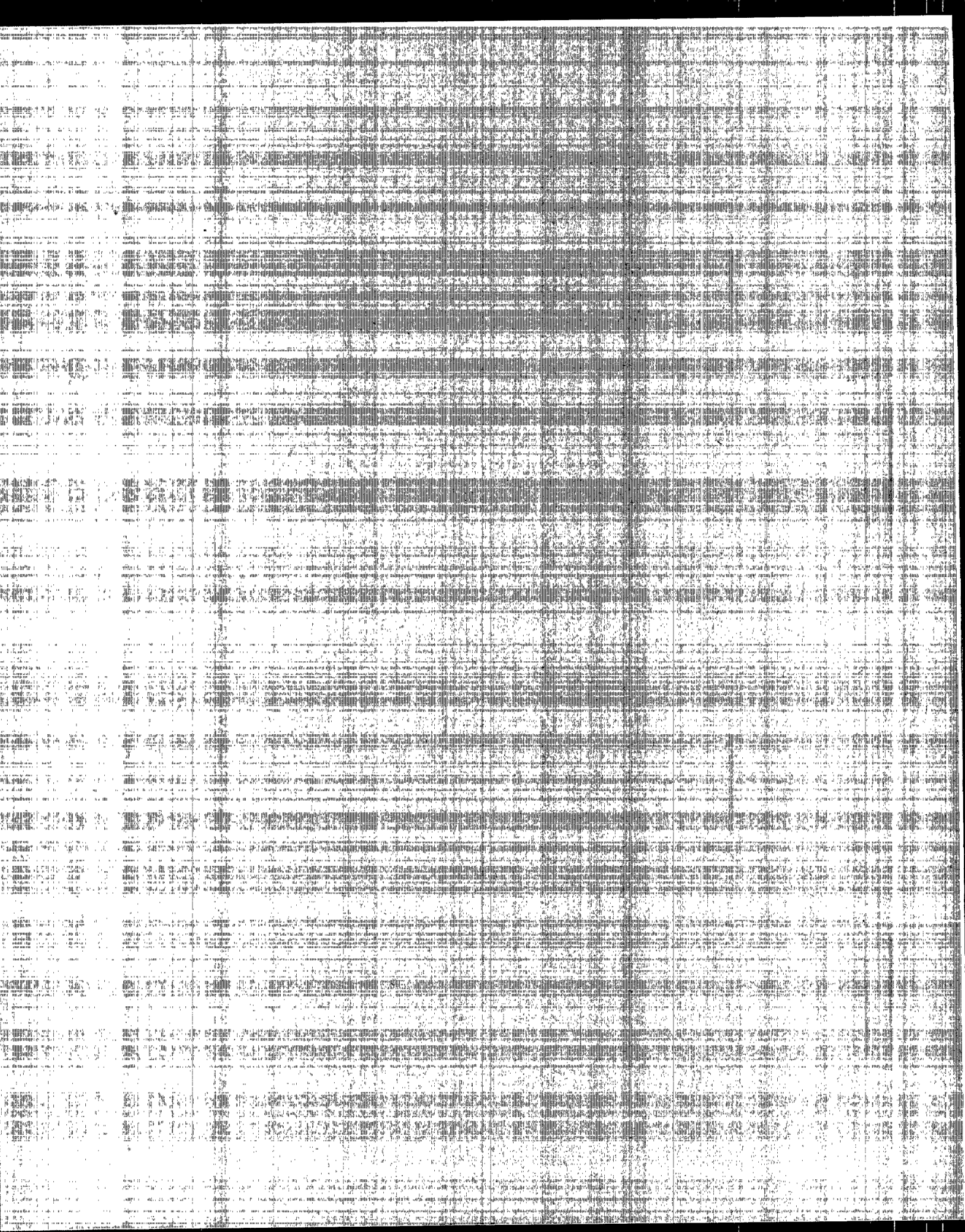
Evaluation of Demonstrated and
Emerging Technologies for the
Treatment of Contaminated Land
and Groundwater (Phase III)

**2001
SPECIAL SESSION**

Performance Verification of In Situ
Remediation Technologies

Number 251

NORTH ATLANTIC TREATY ORGANIZATION



NATO/CCMS Pilot Study

**Evaluation of Demonstrated and Emerging
Technologies for the Treatment of Contaminated
Land and Groundwater (Phase III)**

**2001
SPECIAL SESSION**

**Performance Verification of In Situ
Remediation Technologies**

**Liège, Belgium
September 10-14, 2001**

March 2002

NOTICE

This Annual Report was prepared under the auspices of the North Atlantic Treaty Organization's Committee on the Challenges of Modern Society (NATO/CCMS) as a service to the technical community by the United States Environmental Protection Agency (U.S. EPA). The report was funded by U.S. EPA's Technology Innovation Office. The report was produced by Environmental Management Support, Inc., of Silver Spring, Maryland, under U.S. EPA contract 68-W-00-084. Mention of trade names or specific applications does not imply endorsement or acceptance by U.S. EPA.

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INTRODUCTION

The Council of the North Atlantic Treaty Organization (NATO) established the Committee on the Challenges of Modern Society (CCMS) in 1969. CCMS was charged with developing meaningful programs to share information among countries on environmental and societal issues that complement other international endeavors and to provide leadership in solving specific problems of the human environment. A fundamental precept of CCMS involves the transfer of technological and scientific solutions among nations with similar environmental challenges.

The management of contaminated land and groundwater is a universal problem among industrialized countries, requiring the use of existing, emerging, innovative, and cost-effective technologies. This document reports on the fourth meeting of the Phase III Pilot Study on the Evaluation of Demonstrated and Emerging Technologies for the Treatment and Clean Up of Contaminated Land and Groundwater. The United States is the lead country for the Pilot Study, and Germany and The Netherlands are the Co-Pilot countries. The first phase was successfully concluded in 1991, and the results were published in three volumes. The second phase, which expanded to include newly emerging technologies, was concluded in 1997; final reports documenting 52 completed projects and the participation of 14 countries were published in June 1998. Through these pilot studies, critical technical information was made available to participating countries and the world community.

The Phase III study focuses on the technologies for treating contaminated land and groundwater. This Phase is addressing issues of sustainability, environmental merit, and cost-effectiveness, in addition to continued emphasis on emerging remediation technologies. The objectives of the study are to critically evaluate technologies, promote the appropriate use of technologies, use information technology systems to disseminate the products, and to foster innovative thinking in the area of contaminated land. The Phase III Mission Statement is provided at the end of this report.

The Phase III pilot study meetings were hosted by several countries and at each meeting, a special session was held for the discussion of a specific technical topic. The meeting dates and locations were:

- February 23-27, 1998: Vienna, Austria
- May 9-14, 1999: Angers, France
- June 26-30, 2000: Wiesbaden, Germany
- September 9-14, 2001: Liège, Belgium

The special session topics were:

- Treatment walls and permeable reactive barriers (Vienna)
- Monitored natural attenuation (Angers)
- Decision support tools (Wiesbaden)
- Validation of in situ remediation performance (Liège)

This and many of the Pilot Study reports are available online at <http://www.nato.int/ccms/> and <http://www.clu-in.org/intup.htm>. General information on the NATO/CCMS Pilot Study may be obtained from the country representatives listed at the end of the report. Further information on the presentations in this special session report should be obtained from the individual authors.

Stephen C. James
Walter W. Kovalick, Jr., Ph.D.
Co-Directors

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EXECUTIVE SUMMARY

Robert L. Siegrist¹ and Bert Satijn²

Subsurface contamination by toxic chemicals, including natural and synthetic organic compounds and heavy metals, is a widespread problem at industrial and military sites around the world. At many contaminated sites, there is a sufficiently serious current or future risk to public health and environmental quality such that remediation is warranted. To eliminate a current or future risk, remediation approaches increasingly employ *in situ* technologies comprised of engineered as well as natural attenuation systems. In situ remediation in source areas of contaminated soil and groundwater can be accomplished using mass transfer and recovery methods such as soil vapor extraction, air sparging, and surfactant/cosolvent flushing. In destruction methods can also be employed such as bioremediation and chemical oxidation/reduction. These source area treatment methods can sometimes be enabled by techniques such as soil mixing, soil fracturing, and soil heating. Ground water plumes can be treated by some of these methods as well as through natural biogeochemical attenuation. Finally, for the control of the leading edge of ground water plumes, treatment walls and permeable reactive barriers can be applied.

As site cleanup goals are established (whether it be by a quantitative risk assessment or another method), one must delineate the current nature and extent of contamination in the subsurface and also the desired end-state after in situ treatment has been completed (e.g., risk-based concentrations throughout a volume of soil). Then, the needed technology performance with respect to the contaminant concentration, mass, mobility or toxicity must often be prescribed to achieve the risk reduction judged necessary. Verifying (or validating) potential performance capabilities can be based on process theory, research, and full-scale implementation and nationally standardized test programs (e.g., U.S. EPA Superfund Innovative Technology Evaluation (SITE) program). Verifying actual performance achieved at a specific contaminated site is necessarily based on measurements made at that site to quantify treatment effects that result in changes in contaminant concentration, mass, mobility, and/or toxicity as well as environmental conditions indicative that the desired treatment is occurring.

Verifying that the treatment performance goals set for an in situ remediation technology have been achieved at a specific site is very challenging due to several factors. In general, the effective verification of in situ performance at a particular site becomes more and more challenging with: increasing site size and heterogeneity, presence of dense nonaqueous phase liquids (DNAPLs), cleanup goals that involve high mass removals of contaminants or very low levels of residual contaminants, and remediation technologies that require long time frames and don't readily permit mass balances.

In this Special Session of the NATO/CCMS Pilot Study on the Evaluation of Demonstrated and Emerging Technologies for the Treatment and Cleanup of Contaminated Land and Groundwater (Phase III), was focused on "Validation of Performance of In Situ Remediation Technologies." During this 1.5-day session, there were 14 presentations made. The initial afternoon of the session was devoted to an introduction to the topic (Bert Satijn, The Netherlands) and an overview of process features and challenges (Bob Siegrist, USA). There were also presentations on the needs, views and concerns of the regulators (Victor Dries, Belgium), the site owners (Terry Walden, UK), and the insurance companies (Dominique Ranson, Belgium). The second day was focused on site-specific validation of several technologies including soil vapor extraction (Michael Altenbockum and Oliver Kraft, Germany), surfactant/cosolvent flushing (Leland Vane, USA), bioremediation (Frank Volkering, The Netherlands), chemical oxidation (Robert Siegrist, USA), and permeable reactive barriers (Volker Birke, Germany). These presentations were followed by a presentation on the site-specific validation of in situ remediation at sites with dense nonaqueous phase liquids (DNAPLs) (Arun Gavaskar, USA). The special session was

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to end with a presentation on future developments including expectations, instruments, and goals, The Netherlands) followed by an open discussion period. However, this period was not nearly as productive as it might have been, as the news of the tragic terrorist attacks in the USA became known and attention was refocused on the events of the day.

Based on the presentations made during the Special Session and the discussions that occurred during the meeting, several concepts emerged with regard to validating in situ remediation performance. The co-chairs of the Special Session (Siegrist and Satijn) captured the following concepts that appeared to be recurring themes during the presentations and discussions:

- Verifying (or validating) potential performance capabilities is not the same as verifying actual performance achieved.
- The right combination of several in situ techniques in place and time will often provide the best solution. In this case the verification of the processes is even more challenging. It may also be appropriate to combine in situ methods with ex-situ techniques in a proper way to achieve the most cost efficient result.
- Engineers, regulators, site owners and others need to set realistic goals for in situ remediation and the methods for verifying performance achieved at a particular site. We need to set realistic expectations, which we can, deliver on and defend.
- Clean up of the 3-dimensional subsurface completely to a specific performance goal is challenging, and it is unreasonable to expect that every cubic meter of treated soil will be at or below a target goal.
- Validation requires careful application of monitoring and measurement methods, and methods must be applied to deal with uncertainty. Subsurface investigations that rely on soil sampling and analyses are generally poor and need improvement. Existing, as well as new and more sophisticated, techniques need to be integrated and used to provide multiple lines of evidence enabling conclusions to be made regarding performance goal achievement.
- In situ remediation technologies should be designed and implemented at a particular site to enable performance verification to be achieved.

This report includes the visuals used during the presentations made at the NATO/CCMS meeting in Liège, Belgium on September 10-11, 2001. In most cases, these presentation materials have been supplemented with an extended abstract or paper. Individuals who are interested in learning more on the subject of an individual presentation or on the Special Session should feel free to contact the participants at the address listed in the back of this report.

We would like to acknowledge the participants in this Special Session for their efforts in preparing insightful presentations and contributing papers and presentation materials to this report. We are also grateful to the input and support received from Steve James, Walter Kovalick, Volker Francius, and John Moerlins.

PRESENTATIONS AT THE SPECIAL SESSION

INTRODUCTION TO THE TOPIC AND THE SPECIAL SESSION

Bert Satijn¹

1. INTRODUCTION

Validation of in situ remediation techniques is the topic for this NATO/CCMS Special Session. Before going into the technical aspects, it is necessary to agree on the definition of the word "validation", which in this Special Session, may be used interchangeably with "verification". Validation (or verification) could be defined as a protocolized method to determine the performance of a remediation technology, applying quantitative criteria. So in simple words: *to prove that it is working*.

In many projects the validation of the performance of a remediation system starts at the end of the remediation technique, but in fact it should start with the soil investigation and the design of the remediation system. Important questions are:

1. Do I have a complete view on:
 - a. the site-specific conditions of soil, groundwater, contaminations, subsoil processes of migration and attenuation;
 - b. function (present and future);
 - c. risk profiles of the site;
 - d. the boundary conditions for a clean-up;
 - e. and especially the goal for remediation (preferably in semi-quantitative criteria).
2. What system of remediation could be successful and cost effective? Normally we are thinking of applying one technique, but it often becomes clearer that the right combination of techniques, depth and time-dependent, provides most probably the most cost-efficient solution. A combination of in-situ processes creates an extra challenge for the validation.
3. How will the exploitation of the remediation system be organized? Which steering parameters will be measured and how will they be used?

So the validation process is the last in a chain of activities and depending very much on the first steps. Before going into the discussion on validation, first some statements on the in-situ techniques will be made.

2. STATE OF THE ART OF IN SITU TECHNOLOGIES

In-situ techniques for remediation are relatively new. In the U.S., Germany, the Netherlands and some other countries, our experience is not more than ten years. It started with the pump and treat systems that became in many cases pump & spill. The reason for this was that we didn't understand the relation between diffusion and advection processes, and determining the effectiveness of cleanup by pumping alone.

The goals for in situ techniques are not always realistic, as they can be set by an opportunistic consultant. Subsoil processes in biogeochemistry are not well understood. The complexity of processes in biogeochemistry is high and not easy to monitor. The depth, the simple monitoring devices, and related costs are important factors that explain why there is always a lack of enough data, both in space and time. Heterogeneity is our challenge, on the mm-, cm- and m-scale. Results of the monitoring system are seldom smoothly declining graphs. Uncertainties about the effect of remediation activities are stuff for long discussions between the stakeholders. Soil is heterogeneous while legislation and criteria do not know how to deal with uncertainties and fluctuating results. There is a big gap between policy and

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legislation on the one hand and the practical possibilities on the other hand. Lack of long term monitoring results and thorough evaluations of in-situ techniques can hinder good performance testing and validation of these techniques.

3. VALIDATION OF IN SITU TECHNOLOGIES

The question at hand is, "How to prove that the in-situ technique is working?" There are several methods and approaches that, in combination, can provide information on the performance of an in situ technology at a specific site and support its validation:

- Reduction of concentrations, macroparameters and microparameters;
- Change of process conditions, redox, temperature, Ec, etc.;
- Mass flux reduction;
- Restoration of ecosystem (e.g., nematodes);
- Isotope analyses and other specific analyses; and
- Risk reduction

In the technical sessions various approaches for validation and performance testing will be presented. But the following statements could be made as key issues for this special session:

- Subsoil processes in biogeochemistry have to be studied in more detail:
 - Macro-parameters versus micro-parameters;
 - Primary processes versus secondary processes;
 - Optimization of combination of physical, chemical and biochemical processes.
- Thorough evaluations and verification programs including proper validation do have to provide the performance indicators and bottlenecks;
- Development of monitoring devices has to lead to technologies and methods that provide more, better and cheaper data; and
- The needs and criteria of regulators and site owners have to be translated into validation and verification concepts that deal with field heterogeneity, but nevertheless fit into legislation and performance criteria.

4. PRESENTATION VISUALS ~ presented by Bert Satijn

NATO/CCMS Special Session

Validation of *In Situ* Remediation Performance

Introduction to the session

Bert Satijn

16-08-01 NATO/CCMS special session 1

Introduction of the session

- Validation of in situ techniques
 - to prove that it is working
- State of the Art of in situ techniques
 - Relatively new technology
 - Complex processes in biogeochemistry
 - Heterogeneity is our challenge

16-08-01 NATO/CCMS special session 2

Introduction of the session (2)

- How to prove that the in situ technique is working
 - Validation of Concentrations
 - Validation of reduction
 - Validation of transformation
 - Validation of transport
- How to prove that the in situ technique is working
 - Validation of Concentrations
 - Validation of reduction
 - Validation of transformation
 - Validation of transport

16-08-01 NATO/CCMS special session 3

Program Monday Afternoon

- 13:30 – 13:45 Introduction to the session
Bert Satijn
- 13:45 – 14:30 Challenges for validation
Robert Siegrist
- 14:30 – 15:00 The needs, views and concerns from the regulators
Peter Hertz
- 15:00 – 15:30 Break

16-08-01 NATO/CCMS special session 4

Program Monday Afternoon

- 15:30 – 16:00 The needs, views and concerns from the site visitors
Tony Wadden
- 16:00 – 16:30 The needs and context for the in situ techniques
Robert Siegrist
- 16:30 – 17:00 The needs, views and concerns from the regulators
Peter Hertz

16-08-01 NATO/CCMS special session 5

VERIFICATION OF IN SITU REMEDIATION PERFORMANCE: PROCESS FEATURES AND CHALLENGES

Robert L. Siegrist¹

1. CONTAMINATED SITES AND RISK MANAGEMENT

Subsurface contamination by toxic chemicals is a widespread problem in soil and ground water at industrial and military sites in the U.S. and around the world (NRC 1994, NRC 1997, USEPA 1997, Visser 1993, CARACAS 1998, NATO 1999a). Organic chemicals are often the primary contaminants of concern (COCs) and they commonly include volatile organic chemicals (VOCs) such as tetrachloroethene, trichloroethene, and benzene, and semivolatile organic chemicals (SVOCs) such as polyaromatic hydrocarbons and pesticides (Riley *et al.* 1992, Siegrist and Van Ee 1994, ATSDR 1999, USEPA 1997). In addition, there may be metals (e.g., Pb, Cr) and radionuclides (U, Tc) as co-contaminants of concern (Evanko and Dzombak 1997).

In the beginning, when contaminated sites were first discovered and their potential impacts on human health and environmental quality were first revealed, appreciable levels of hazardous chemicals in uncontrolled environmental settings (e.g., soil or groundwater) were presumed to present a condition in need of action and implicitly, an unacceptable risk. Risk reduction was typically achieved by excavation of soil and waste with subsequent treatment and disposal offsite, combined with pump and treatment of contaminated groundwater (Mackay and Cherry 1989, USEPA 1997, USEPA 1999). Now more explicit risk assessment and management underpins cleanup programs for Superfund and most other contaminated sites (USEPA 1989, Labieniec *et al.* 1996, Sheldon *et al.* 1997, CARACAS 1998). Baseline risk assessments are first completed to define the need for and extent of site cleanup and to develop site specific remediation alternatives to mitigate unacceptable risks to an agreed upon goal. Generic, rather than site-specific, risk assessments can also be done to develop screening level criteria for assessing sites and establishing cleanup goals (e.g., Visser 1993, USEPA 1996).

Varied exposure scenarios can present serious current or future risks at many contaminated sites. At many sites, risk is often governed by human exposures to chemicals in drinking water. Such contamination has commonly resulted from wastes released at or near the land surface and the subsequent migration of chemicals through soil into the underlying ground water (Figure 1).

To mitigate current or future risks, remediation approaches increasingly employ in situ technologies comprised of engineered as well as natural attenuation systems (Figure 2) (NRC 1994, NRC 1997, USEPA 1997, NATO 1998, NATO 1999a,b, Siegrist *et al.* 2001). In situ remediation in source areas of contaminated soil and groundwater is being accomplished using mass transfer and recovery methods (e.g., soil vapor extraction, air sparging, surfactant/cosolvent flushing) and in place destruction methods (e.g., bioremediation, oxidation/reduction), sometimes aided by enabling techniques (e.g., soil mixing or fracturing, soil heating). For treatment of the distal regions of groundwater plumes, natural biogeochemical attenuation and permeable reactive barriers are being employed.

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Figure 1: Illustration of a common contaminated site scenario where land disposal of industrial wastes has led to organic chemicals leaching into the subsurface being transported to receptors exposed by ingestion of contaminated drinking water or inhalation of vapors.

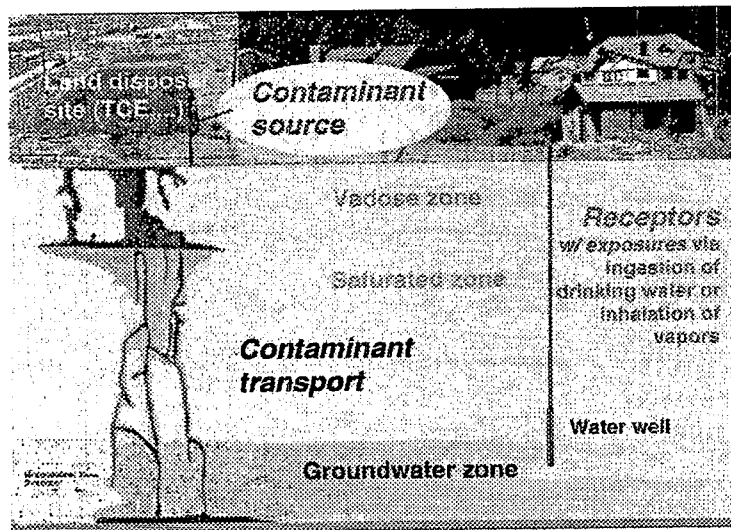
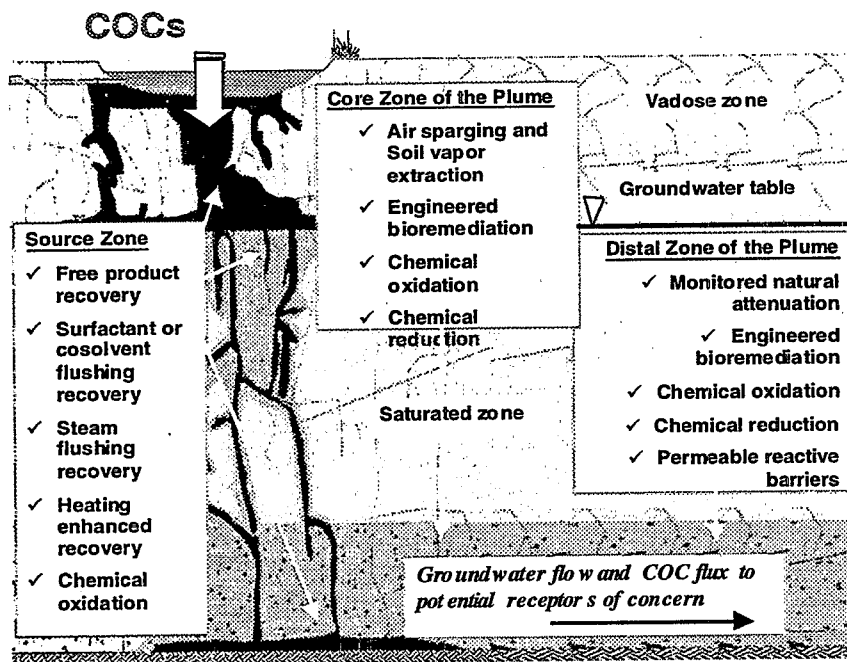


Figure 2: Remediation approaches for in situ application at a typical contaminated site such as illustrated in Figure 1 (after Siegrist *et al.* 2001).



2. VERIFICATION OF PERFORMANCE POTENTIAL VS. SITE-SPECIFIC ACHIEVEMENT

Risk reduction can be achieved using in situ remediation technologies by treating the COCs and decreasing their concentrations, mass, mobility and/or toxicity. Verification that risk has in fact been reduced to a target level established using a site-specific risk assessment or application of screening-level cleanup criteria is based on a quantitative assessment of technology performance. In its broadest sense, technology performance encompasses more than just treatment efficiency and risk reduction. In general, it may be defined as: "Performance is a measure of a technology application with respect to a specified function". Example functions include:

- Treatment efficiency (and risk reduction),
- Ease of implementation,
- Degree of site disruption and aesthetic impact,
- Compatibility with long-term land use plans, and
- Cost effectiveness.

Technology performance with respect to treatment efficiency is of concern in this paper and NATO special session. Treatment efficiency and risk reduction must necessarily be incorporated into remediation practice, either implicitly or explicitly. As site cleanup goals are established (whether it be by a quantitative risk assessment or another method), one must delineate the current nature and extent of contamination in environmental media throughout some location in space and time and also the desired end-state after treatment (e.g., risk-based concentrations throughout a volume of soil). Then, the needed technology performance with respect to the contaminant concentration, mass, mobility or toxicity must be prescribed to achieve the risk reduction judged necessary (e.g., treatment to reduce COC levels below drinking water limits). Technology performance goals related to treatment are thus set such that achieving them would enable overall site cleanup to be realized.

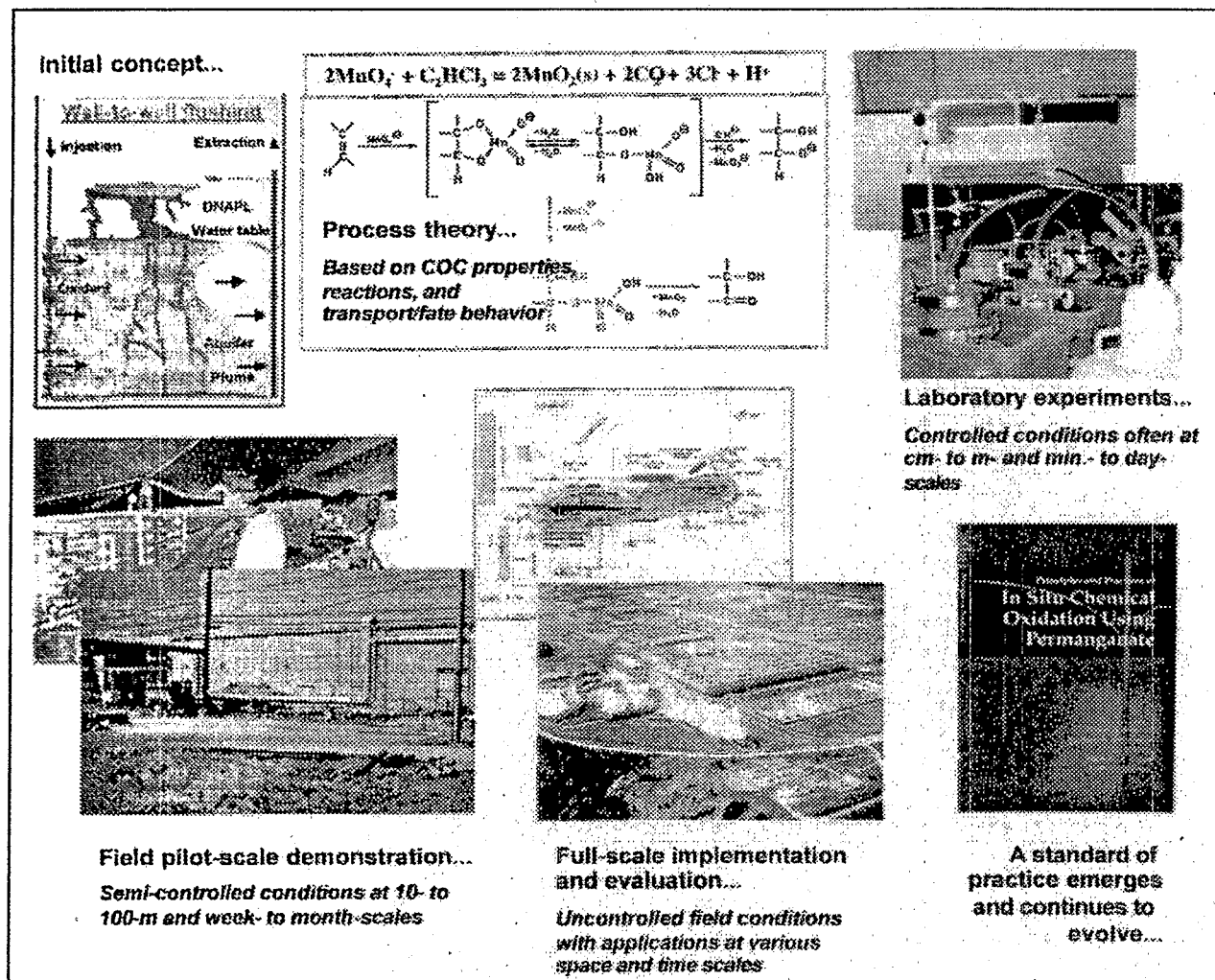
Verifying (or validating) *potential performance capabilities* is not the same as *verifying actual performance achieved*. Potential performance capabilities can be established based on knowledge gained from different methods and scales of realization (Figure 3). Performance potential is often initially projected based on an initial treatment concept, along with process theory based on contaminant properties and site characteristics. An example is the projection of potential performance of soil vapor extraction to remove volatile organic compounds from unsaturated, permeable soils located above the ground water table. Understanding and confidence in potential performance can be increased through confirmatory testing and evaluation completed during laboratory testing and field pilot-scale demonstrations as well as through full-scale implementation and nationally standardized test programs (e.g., U.S. EPA Superfund Innovative Technology Evaluation (SITE) program). As technology implementation occurs at a large number of sites, a standard of practice can emerge and continue to evolve.

Verifying actual performance achieved at a specific contaminated site is necessarily based on measurements made at that site to quantify treatment effects that result in reduced risk. Assessment of technology performance related to risk reduction are often based on quantifying changes in contaminant concentration, mass, mobility, and/or toxicity as well as environmental conditions indicative that the desired treatment is occurring. Verifying that the treatment performance goals set for an in situ remediation technology have been achieved at a specific site is very challenging due to several factors. Contaminants often have complex and uncertain distributions among multiple phases (e.g., vapor, aqueous, solid, and non-aqueous liquid) and over time and space in the subsurface. This results in great difficulties to interpolate and accurately estimate values at unobserved locations. Verification of performance achievement to reach stringent cleanup goals (e.g., the 5 ug/L U.S. drinking water standard for trichloroethylene (TCE)) can be challenging due to the small range for error and uncertainty (i.e., 0 to 5 ug/L) in estimating that treatment has achieved the goal. Finally, some treatment technologies can

constrain the viability of performance verification methods due to their process function and treatment-induced heterogeneities (e.g., inability to close a mass balance on COCs, development of preferential pathways).

In general, the effective verification of in situ performance at a particular site becomes more and more challenging with: (1) increasing site size and heterogeneity, (2) presence of dense nonaqueous phase liquids (DNAPLs), (3) cleanup goals that involve high mass removals of contaminants or very low levels of residual contaminants, and (4) remediation technologies that require long time frames and don't readily permit mass balances.

Figure 3: Methods and scales of information gain during development of an understanding of the *potential performance capabilities* of in situ remediation technologies.



3. APPROACHES TO SITE-SPECIFIC PERFORMANCE VERIFICATION

Verifying actual performance achieved at a specific contaminated site must often be accomplished by quantifying, to some degree of certainty, changes in contaminant concentration, mass, mobility, and/or toxicity as well as environmental conditions consistent with treatment process function. These approaches are highlighted below.

3.1 Quantifying Contaminant Concentrations

A common cleanup goal for contaminated ground water can be drinking water standards (e.g., 5 ug/L TCE). At a specific site where this cleanup goal might be set for a nearby drinking water well, the technology performance goal could be to decrease the concentrations of TCE to some target level in soil and/or ground water within the contaminated site boundaries so that natural attenuation would yield a concentration at or below drinking water standards at the nearby drinking water well. Performance verification for this goal normally would involve sampling at multiple locations and times with analyses for the COC of interest. The resulting dataset would then be subjected to statistical analysis to enable comparison of post-treatment conditions to the goal of 5 ug/L TCE. Potential problems and challenges with this type of goal and verification approach include (1) the need for large numbers of samples to address site heterogeneities and temporal and spatial variability, (2) the potential for large measurement errors with some COCs in some media (e.g., volatile organic compounds in soil), (3) the potential errors in interpolation methods used to estimate levels at locations without measurements, and (4) the fact that concentration changes may not be due to in situ treatment (e.g., changes could be due to rate-limited processes and dilution effects during in situ flushing or extraction technologies). These problems and challenges can be overcome, at least in part, by careful and integrated use of modern sampling and analyses methods, field analytical methods, in situ sensor technologies, and geostatistical modeling methods (Crumbling *et al.* 2001, NATO 2001).

3.2 Quantifying Contaminant Mass

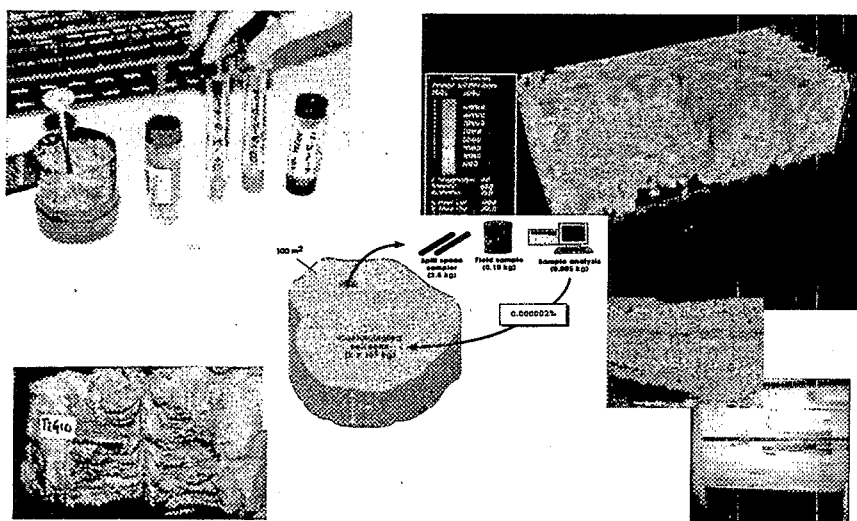
Another type of cleanup goal is to decrease the mass of COCs to a target level within a specified region of the subsurface such that the release rate for contaminants to soil gas or ground water is reduced to an acceptable rate (often a rate that results in no further growth or even contraction of plumes with concentrations in them being below a set value). To enable application of this type of goal, the COC mass present before and after treatment must be determined and this is normally done by characterizing contaminant concentrations and multiplying them by the volume of media and its density. The COC mass reduction is then estimated by comparing the post-treatment mass to the pre-treatment mass. Verifying that a specified mass reduction (e.g., 90%) has been achieved requires the same elements as required for quantifying contaminant concentration changes (see Section 3.1). In addition, it requires knowledge of the media volume and density. Potential problems and challenges with quantifying contaminant mass include the same ones confronting quantification of contaminant concentrations, namely: (1) COCs can be distributed in a complex manner among phases and in vertical and horizontal dimensions, (2) the potential for large measurement errors with some COCs in some media (e.g., volatile organic compounds in soil), (3) the potential errors in interpolation methods used to estimate levels at locations without measurements, (4) the fact that concentration changes may not be due to in situ treatment, but also (5) the added fact that in situ remediation can alter subsurface conditions and make comparison of post-treatment masses invalid (e.g., treatment-induced mobilization of DNAPLs). As noted previously, these problems and challenges can be overcome by careful and integrated use of modern sampling and analyses methods, field analytical methods, in situ sensor technologies, and geostatistical modeling methods. In addition, at sites contaminated by DNAPLs, diagnostic tools such as partitioning tracers represent a group of methods that can interrogate the subsurface and potentially provide a more accurate estimate of contaminant mass within a volume of the subsurface as compared to that provided by discrete samples and geostatistical analyses. Other emerging methods that enable integrated assessment of subsurface regions include large-scale pump tests and mass flux meter techniques.

3.3 Quantifying Contaminant Mobility

Quantifying contaminant mobility traditionally has been applied to characterize leachability of COCs from solid media such as soil, sediments, debris, or waste products. This is normally done using various laboratory leaching procedures such as the U.S. EPA toxicity characteristics leaching procedure (TCLP). However, quantifying COC mobility can also be used to assess the risk reduction achieved by changes in

concentrations in plumes emanating from source areas. For example, at sites contaminated by DNAPLs, depending on the DNAPL properties and subsurface distribution along with the site heterogeneities and ground water flow regime, reducing the initial DNAPL mass present by some amount (but not necessarily 100%) can reduce the mass flux from the DNAPL and thereby reduce the concentration in the ground water plume to a specified goal. Many of the same problems and challenges that confront efforts to quantify contaminant concentrations and mass also confront assessment of COC mobility. Likewise, the same approaches to overcome limitations are also available.

Figure 4: Classic approach to quantifying COC concentrations by discrete sampling and analyses to enable geostatistical modeling of COC concentration and mass distributions, and the basis for error and uncertainty due to complex subsurface conditions and site heterogeneities.



3.4 Quantifying Contaminant Toxicity

Performance goals can be targeted at changing COC toxicity through treatment to some target level in soil and/or ground water within some region of the subsurface. One example of such a goal is in situ treatment to transform 100% of the chromium in soil from Cr^{+6} to the less toxic, Cr^{+3} . In addition to the problems and challenges associated with quantifying concentrations or mass in the subsurface, there can be questions about verifying long-term stability of the observed toxicity reduction effect. This requires long-term testing or sufficient fundamental understanding to predict long-term effects with certainty.

3.5 Supporting Measures

Measurements and observations of conditions that are indicative that in situ treatment is being accomplished can also be used to aid verification of in situ remediation technology performance. Examples of these types of supporting measures include: (1) remote sensing and geophysical mapping of treatment agent (or effect) delivery into a subsurface zone to be remediated, (2) measurement of biogeochemical conditions indicative of treatment process function (e.g., pH, Eh, dissolved oxygen, microbial activity, matrix chemistry), and (3) measurement of reaction products (e.g., CO_2 produced by biodegradation of petroleum hydrocarbons or chloride ions produced by oxidative degradation of TCE).

4. SUMMARY

In situ treatment technologies are increasingly being considered for remediation of contaminated sites, yet questions remain regarding how one can effectively and reliably verify performance. Verification of performance of in situ technologies and the achievement of cleanup goals at a specific site can be extremely challenging for many reasons, most notably perhaps, due to the complex distributions of contaminants in multiple phases over space and time in the subsurface and the difficulties to interpolate and accurately estimate values at unobserved locations. Multiple types of data that demonstrate one or more measures of treatment effectiveness (i.e., reduction in concentration, mass, mobility, and/or toxicity) are normally needed to effectively verify treatment performance at a particular site. In acquiring these data, careful application of multiple monitoring and measurement approaches and methodologies is critical to ensure that the proper data are collected and sufficiently comprehensive and accurate for the intended purpose. As one contemplates in situ remediation and the verification of performance at a particular site, questions emerge such as:

“What are realistic expectations for verification of in situ performance? For example, is 95% mass removal with 90% confidence a reasonable expectation?”

“What is the best verification approach for a given type of in situ remediation technology and site-specific performance goal?”

“What is an appropriate level of investment in verification at a particular site? For example, is 5% of total project cost appropriate? What about 15% or 30%?”

“Should the choice of an in situ technology for a specific site depend on the ability to effectively verify performance at that site?”

As the practice of in situ remediation continues to evolve and field experiences are complemented by the results of research and development efforts, answers to these and related questions will hopefully emerge.

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6. PRESENTATION VISUALS ~ presented by Robert L. Siegrist


Validation of In Situ Remediation Performance ~ An Overview

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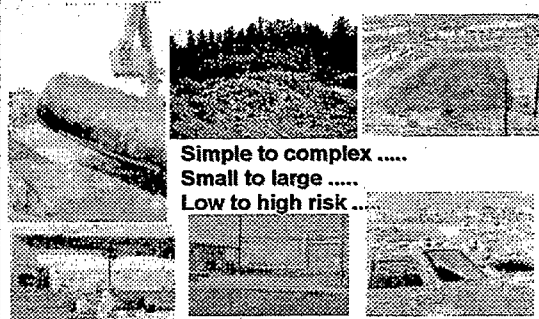
NATO/CCMS Country Representatives Meeting
 Liege, Belgium
 9-14 September 2001

Opening Remarks

- Presentation scope**
 - Contaminated sites and risk-based management
 - In situ remediation technologies
 - Technology performance and goals
 - Methods for validating performance goal achievement for in situ technologies



Contaminated Sites



Simple to complex
 Small to large
 Low to high risk

Site location and proximity to receptors

Size and geometry of contaminated media

- Small volumes of shallow contaminated soil
- Large, deep groundwater plumes

Subsurface properties

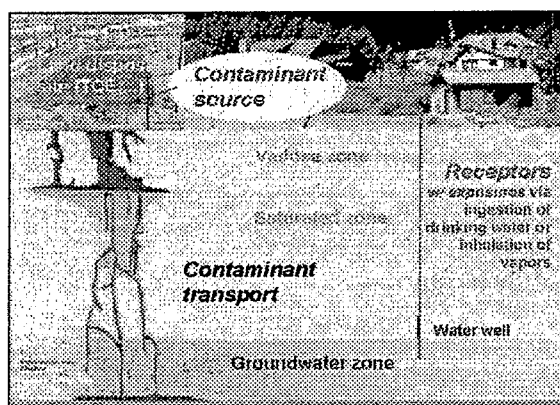
- Groundwater in sands vs. layered sediments vs. fractured rock
- Unsaturated sandy soil vs. low permeability media vs. fill

Contaminant type and properties

- Organics vs. metals; simple vs. complex mixtures
- Contaminant volatility, solubility, and reactivity

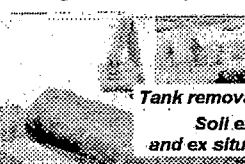
Contaminant distribution in the subsurface

- Distribution among phases (NAPL, sorbed, aqueous, vapor)
- Distribution in horizontal and vertical dimensions



Remediation Practice

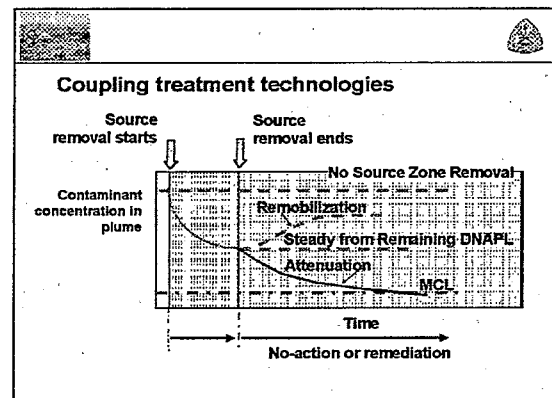
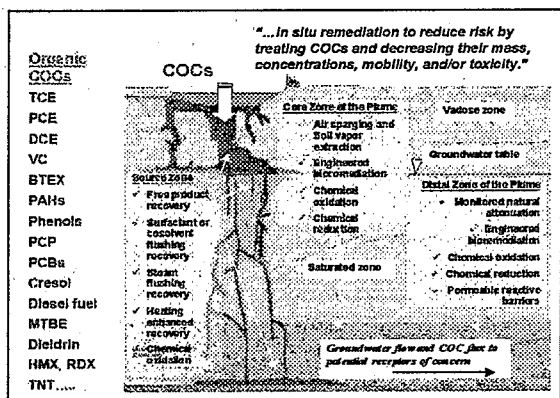
Leaking tank ... Transport ... Receptors → Risk



Tank removal
 Soil excavation and ex situ disposal

In situ remediation of soil and groundwater...

Groundwater P&T for plume containment ...



Technology Performance

What do we mean by "technology performance" ?

"Performance is a measure of a technology application with respect to a specified function"

For example:

- ☐ Treatment efficiency
- ☐ Ease of implementation
- ☐ Site disruption and aesthetics
- ☐ Compatibility with long-term land use
- ☐ Cost effectiveness
- ☐ Other...

How does "technology performance" fit into remediation practice?

Technology Performance

As we set Site cleanup goals we must:

- ☐ Define contamination in environmental media at some location in space and time
e.g., risk-based concentrations throughout a volume of soil
- ☐ Define the needed technology performance with respect to contaminant concentration, mass, mobility and/or toxicity
e.g., treatment to reduce COC levels below drinking water limits

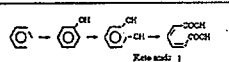
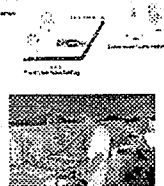
Technology performance goals are set such that achieving them would enable overall site cleanup

Technology Performance

Verifying potential performance capabilities:

- ☐ Based on contaminant and site characteristics and process theory
- ☐ Confirmatory testing and evaluation completed during R&D projects (e.g., Univ. R&D)
- ☐ Standardized testing (e.g., SITE program)
- ☐ Standard of practice established from project implementation at a large number of sites

Validating actual performance achieved at a single, specific contaminated site

Site-Specific Validation

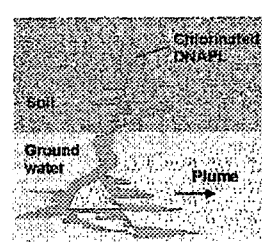
Approaches to validating performance achievement at a specific site are based on:

Quantifying the reductions in contaminant:

concentration, mass, mobility, and/or toxicity

and

Observing conditions indicative of treatment



Site-Specific Validation

Validating that technology performance goals have been achieved at a specific site is very challenging

- ☐ Complex distributions of contaminants among phases and over space in the subsurface
- ☐ Difficulties to interpolate and estimate values at unobserved locations
- ☐ Validation of performance against stringent cleanup goals (e.g., drinking water standards)
- ☐ Treatment technologies can affect the ability to validate in situ performance (e.g., mass recovery vs. destruction)

Site-Specific Validation

In general, the effective validation of in situ performance at a particular site becomes more and more challenging with:

- ☐ Increasing site size and heterogeneity
- ☐ Presence of nonaqueous phase liquids
- ☐ Cleanup goals that involve...
 - ☐ high mass removals of contaminants
 - ☐ very low levels of residual contaminants
- ☐ Remediation technologies that require...
 - ☐ long time frames
 - ☐ don't readily permit mass balances

Site-Specific Validation

Quantifying contaminant concentrations

- ☐ Technology goal is to decrease concentrations to some target level in soil and/or ground water within some region (e.g., yield 5 ppb TCE at the property boundary)
- ☐ Validate performance by media sampling & COC analysis with statistical analysis for comparative purposes
- ☐ Potential problems and challenges ...
 - ☐ Need for large numbers of samples to address site heterogeneities and temporal and spatial variability
 - ☐ Potential for large measurement errors (e.g., VOCs in soil)
 - ☐ Errors in interpolation to estimate levels at locations without measurements
 - ☐ Concentration changes may not be due to treatment (e.g., rate-limited processes, dilution)

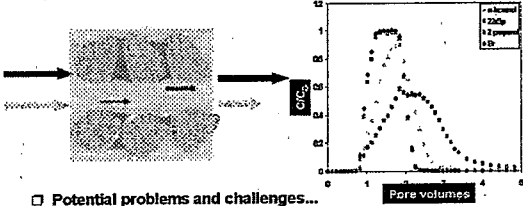
Site-Specific Validation

Quantifying contaminant mass

- ☐ Technology goal is to decrease mass to a target level in a specified region of the subsurface
 - $$\text{COC mass} = \text{Concentration} \times \text{Volume} \times \text{Density}$$
 - $$\text{COC mass reduction} = (\text{COC mass before} - \text{COC mass after})$$
- ☐ Validate performance by media sampling & analysis for COCs with statistical analysis to estimate mass
- ☐ Potential problems and challenges ...
 - ☐ COCs can be distributed in a complex manner among phases and in vertical and horizontal dimensions
 - ☐ Potential for large measurement errors (e.g., VOCs in soil)
 - ☐ Errors in estimated levels at locations without measurements
 - ☐ In situ remediation can alter subsurface conditions and make comparison of post-treatment masses invalid

Site-Specific Validation

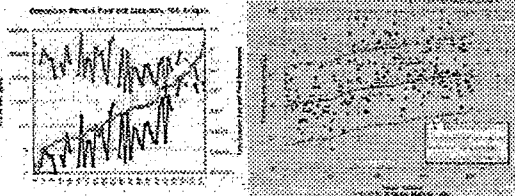
- Validate performance using partitioning tracer tests to determine pre- and post remediation NAPL distributions



Potential problems and challenges...

- Reliability for mixtures in heterogeneous conditions
- Effects of treatment technology on flow and tracer behavior
- Waste generation and cost

Site-Specific Validation

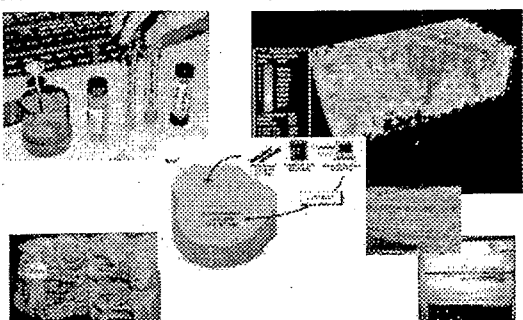


Potential measurement bias due to sampling effects

Uncertainty in geostatistical estimates of concentrations

Error and uncertainty in estimates of concentrations and mass in the subsurface
Overcome by field methods, sensor technologies, spatial modeling, etc.

Site-Specific Validation



Site-Specific Validation

- Quantifying contaminant mobility
 - Technology goal is to decrease mobility of COCs to some target level in soil or waste within some region (e.g., yield 5 ppb TCE in leachate from treated waste)
 - Validate performance by media sampling & testing for COC leachability with statistical analysis for comparative purposes
 - Potential problems and challenges ...
 - Need for large numbers of samples to address site heterogeneities and temporal and spatial variability
 - Potential for large measurement errors (e.g., VOCs in soil)
 - Errors in interpolation to locations without measurements
 - Extrapolating from lab test conditions to realistic long-term field conditions

Site-Specific Validation

- Quantifying contaminant toxicity
 - Technology goal is to decrease toxicity of COC to some target level in soil and/or ground water within some region (e.g., transform 100% of the Chromium from Cr^{6+} to Cr^{3+})
 - Validate performance by media sampling & COC analysis with statistical analysis for comparative purposes
 - Problems and challenges ...
 - Need for large numbers of samples to address site heterogeneities and temporal and spatial variability
 - Potential for large measurement errors (e.g., Eh changes)
 - Errors in interpolation to estimate levels at locations without measurements
 - Assessing long-term stability of observed performance

Site-Specific Validation

- Supporting measures
 - Measurements and observations of treatment conditions other than direct observations of the contaminants being treated in situ
- Examples:
 - Remote sensing and geophysical mapping
 - Measurement of mass recovered (e.g., SVE off-gas)
 - Measurement of reaction products (e.g., Cl^-)
 - Measurement of biogeochemical conditions indicative of treatment process function (e.g., pH, Eh, D.O., microbiology, chemistry,...)

Closing Remarks

- In situ treatment technologies are increasingly being used for remediation
- Validating performance of in situ treatment and achievement of a goal at a specific site can be extremely challenging
- Multiple types of data that demonstrate one or more measures of treatment (concentration, mass, mobility and/or toxicity) are normally needed
- Careful application of multiple monitoring and measurement approaches and methodologies is critical to effective validation at a specific site

Closing Remarks

- Some questions:
 - What are realistic expectations for validation of in situ performance?
e.g., 95% mass removal with 90% confidence
 - What is an appropriate level of investment in validation at a particular site?
e.g., 5% of total project cost? ...15%? ...30%?
 - Should the choice of an in situ technology for a specific site depend on the ability to effectively validate performance at that site?

NEEDS, VIEWS, AND CONCERNS OF THE REGULATORS

Victor Dries¹

1. INTRODUCTION

Soil remediations absorb quite a lot of time and money. Most people don't really adore spending either of these on a factor that doesn't seem to have a positive impact on the future results of the company. Every party concerned is looking eagerly for means to make remediations cheaper and more efficient. In-situ remediation technologies offer quite some advantages: they are often quite a bit cheaper than excavation concepts, you don't spend all of your money at once, but spread payments over quite some years and the use of your land can be more or less continued. In-situ treatment is not evident, though; the soil matrix is very complex and prediction and optimisation of the process is very hard. Problems may arise at several steps in the decision procedure.

2. SOIL INVESTIGATION

Every remediation concept starts with a soil investigation to know whether or not you have to remediate, and to offer the data necessary for the evaluation of different remediation concepts and for the modelling of the chosen concept. Yet, even soil investigations may pose quite a few problems.

2.1 Investigation Problems

Classical soil investigations have a number of limitations. A number of samples are taken on specific places on a site. The information you get out of this is of course only relevant for the place where you take the sample and even then, for the depth where you take the sample. Enough samples give you a quite good idea of a site, but it will never be better than "quite good". You never know you haven't missed a spot, you never know that the concentration of chlorinated solvents is the highest on the depth where you have taken your groundwater sample. Apart of that, the question arises how you organise your site investigation. Mostly, the first investigation (we call it exploratory) gives you a general idea of whether your site is contaminated or not. The next investigation (we call it descriptive) tries to find the boundaries of the pollution. Two procedures may be used to achieve this. Firstly, you tell the investigator to do take as many samples as he likes, as long as you get the result as fast as possible. This may imply quite a large lot of samples, and can be quite expensive. To avoid this, most people prefer a tiered soil investigation, where a round of samples is taken and analysed; based on the results, a next round of samples is taken in the most relevant direction. This procedure is more cost-effective, but takes a lot of time.

2.2 Alternatives

To avoid those problems, alternative detection and analysis technologies can be used, such as so-called intelligent probes, mobile XRF, mobile GC, and geo-radar. Those technologies are still quite young, though, and most still need thorough validation. Even when such a technology is validated, most of the times a few classical samples need to be taken and analysed to verify the obtained data.

2.3 Laboratories

A very critical factor in soil investigations is the quality of the laboratories used. Samples are analysed and the results are used to check whether or not certain standards have been passed or whether the concentrations found pose any risk. A question most people dare not ask is what the relevance is of the data obtained from the lab. In annex to this text, I put the results on organic compounds of a round robin organised about 2 years ago among labs already accredited to analyse different sorts of samples (waste,

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waste water, ...). If the results of the round robin were positive, a lab also got the accreditation to carry out analyses on soil and groundwater. The Flemish regulation implies that laboratories have to be accredited in a double procedure: not only the instruments, personnel and procedures in the lab are evaluated, but also a lab must prove its qualities in a round robin. This round robin was already the second try; the results of the first run were so bad, we couldn't even use the data to do a proper statistical analysis. Even though the labs knew the test was extremely important for them (access or not to a fast growing market of soil analyses) the results were quite poor. Recoveries for e.g. benzene in soil ranged from 4% up to 131%, for styrene from 10% to 182%, for dichloromethane from 1,5% up to 199%, for naphthalene from 0,2% to 128%! In water recoveries ranged e.g. for octane from 3,5% up to 75%, for tetrachloromethane from 62% to 194%, for 1,4 dichlorobenzene from 45% up to 174%, for naphthalene from 17% up to 126%. I want to stress that the samples were all well homogenised and stored in optimal conditions until taken in by the labs. How often is this true during soil investigations?

We were lucky, we found those problems, and we did not accept the labs with bad recoveries for soil or groundwater analyses. Some of the labs we did not accept were quite big foreign labs, which were accredited in their mother country according to "classical" accreditation systems (do you have quality control procedures and do you follow them thoroughly). How many countries, though, have an accreditation system where also the quality of the analyses is evaluated? Those problems forced us to set up a system of blind controls of the laboratories, as we wonder what the quality of an analysis is when a lab is not working for such an important goal as a market entry, but rather under the stress of delivering results as soon as possible. For relatively volatile compounds, the problems are even larger, because it's very hard to prevent loss during sample taking.

A lot of work still has to be done to improve analyses, and we have to view very closely if certain parameters cannot be measured better in the field. What's the use of spending a lot of energy in a thorough risk assessment if even your input is not sure? What guarantee do you get if a risk assessment states that a risk is present, but that it's not really serious?

3. REMEDIATION

The Flemish soil remediation decree states that historical soil pollution needs to be remediated if the soil contamination poses a serious risk for man, groundwater or environment. The moment of the remediation depends on the priority given to the pollution (except when the ground is transferred; then the transfer triggers the remediation). To remediate all historical soil pollution that poses a serious risk, a period until 2036 has been dedicated.

3.1 In-situ Concepts

In situ techniques are applied quite a bit at sites in Flanders, although I am skeptical about the ability of current techniques to offer complete solutions. Pump and treat solutions are generally accepted, but with the proviso that the chances of P & T offering a complete solution are not high. Poor site investigation work often limits P&T effectiveness. Hydrogeological containment is used for managing active waste sites, but is not popular as a remediation approach.

Soil venting and bioventing are popular technologies, and air sparging is growing in importance as a remedial technique, all are well accepted by regulators. A recent study on emissions from these processes indicates that the emissions control is of limited effectiveness, with significant transfer of volatile organic compounds from soil to atmosphere. Currently used *in situ* techniques are not apt to deal with very severe contaminations, as treatment times may span several decades. Most concepts offer not a complete remediation of a site; on the long run, we have to take into account that when the use of the ground changes, the contamination may pose serious risks again and that the future use may be hindered.

I think the new boosting concepts that have been developed in the United States may offer solutions for heavy contaminations, that cannot be solved in an easy way by classical concepts in a relatively short time span. Good care has to be taken of the control of the system, as mobilisation of the contaminant opens also the risk that contamination is spread beyond the present boundaries of the contamination or even of the property.

3.2 Natural Attenuation

A second alternative that looks very attractive is natural attenuation. Just count on the biodegradability of the pollutant, and make sure the pollutant doesn't leave your ground. To check this, a sound monitoring system is installed. Sounds pretty good, but we have to focus on a few problems. Firstly, this monitoring may last many years, thus implying important organisational aspects, as well as a cost that may prove to be quite high on the long term. Secondly, we only accept a concept of attenuation if you can prove that attenuation is taking place and is guaranteed on the long term. As attenuation depends on many factors, a very good knowledge of the soil and of the soil processes is needed. Our experience is that very few consultants have the experience and the know-how to do a good modelling and that the amount of data needed to do this modelling requires a thorough (and expensive) soil investigation. If your problem is quite big, this is no problem of course, but we still have the problem of the monitoring. Above, I already stated that laboratory analyses are not always exact, even for parameters that are more or less common. This problem is even much larger when one has to analyse parameters that are not common at all. A great example is the degradation of chlorinated solvents. I have already heard very nice speeches of consultants indicating that they measure a lot of parameters to prove attenuation is taking place, even vinyl chloride and ethene. I know very few labs capable of analysing these parameters in a proper way. Even when you find one, taking a sample, conserving it properly until it reaches the lab and sample preparation is not evident at all of this case, so it may quite well be that the plume of dissolved product and by-products is much larger than you measure. We are not very likely to accept this if the plume is moving towards a neighbour who is not too far away.

3.3 "Stimulated Attenuation"

I like the term *stimulated attenuation*; however it's just a nice name for existing concepts. Either it's an in situ remediation concept, or an attenuation concept where the source is removed, or a combination of both, where the source is removed and afterwards an in situ treatment of the plume is started. I like them quite a bit better than natural attenuation, because at least you have a decent idea that part of the contamination is removed.

Especially the combination looks quite good, because most often in situ treatment without taking away the source takes ages, and on the other hand a well designed in situ treatment can reduce the term of monitoring with many years. Again, we have to stay critical to try design a treatment and to monitor the plume as well as possibly.

3.4 Isolation Concepts

You can opt for alternative soil remediation technologies that don't take away the pollution in a short term. A first one is isolation of the pollution. By isolation, you break the pathway and reduce the risk. Isolation is quite often much cheaper than removal of the pollution for very large contaminations, but has some disadvantages. Firstly, an isolation always implies a duty of care: whatever you do on a ground, you have to take care that you don't break the isolation. This may pose problems, for instance when you want to construct a new building on the ground.

You have to take into account that the isolation has to be maintained; this can make foundations quite a bit more complex (and thus more expensive). This also impacts the value of a ground when you want to sell it. Secondly, each isolation needs to be monitored to make sure the isolation is still functioning well. This monitoring is strictly spoken eternal; this implies important organisational aspects to make sure the monitoring is assured and may imply important costs. Another disadvantage is that every isolation is temporal: after a while the isolation will break down. I know of no system that has eternal life. A good choice of the isolation concept is extremely important; as a basic principle, one can state that every more or less "natural" system is safer than artificial concepts. To reduce infiltration of rain in a polluted area, I trust more in a well-designed natural vegetation system than in an HDPE-liner. Producers of liners currently use a 40 year-guarantee for their products, when their products are properly placed. A good control of the installation of a liner is extremely important, but also extremely difficult. We have already encountered landfills which had been covered 7 years ago and needed remediation, because the liner was not properly installed. Even if the liner is properly installed, you have to be aware that after 40 years, your isolation is quite likely to break down.

An isolation concept I really adore, are active walls. Firstly, the contamination is isolated; thus making sure it poses no unacceptable risks for the surroundings. Where classical isolation concepts tend to be almost eternal and require a good control of the permeability of the wall, the groundwater in this concept can stream quite freely, as long as we are sure it passes through a treatment zone. Thus permeability demands of the wall are a bit less stringent, the wall is quite often quite a bit cheaper, and in a middle-long run most of the mobile fractions of the contamination moves through the active zone, where it is remediated. Again we have to be aware that modelling of an active wall is not very easy, as you have to know what processes you need in your wall. Such a wall also demands maintenance and sound monitoring. The monitoring though may depend of the level of "self-control" the system can deliver. A good concept of the wall can make sure that all contaminated water has to pass through the active zone, and then monitoring of the activity of the zone can be more effective than monitoring behind the wall. In this case, monitoring of the groundwater downstream of the wall can be reduced strongly.

4. CONCLUSIONS

I like in-situ remediation technologies quite a bit. They have quite some advantages: they are often quite a bit cheaper than excavation concepts, you don't spend all of your money at once, but spread payments over quite some years and the use of your land can be more or less continued. We have to spend enough attention to good soil investigation and risk evaluation, as those are the basis to decide whether or not soil remediation is necessary and how the risks can be controlled and reduced in the most effective way. We have to be very careful, as risk evaluation by models seems to be quite exact, but many doubts remain. One of the larger problems is the lack of guarantee offered by laboratory analysis.

Soil remediation is expensive, so we try to look for most cost-effective remediation concepts. Isolation seems quite interesting for large contaminations in the short run, but it may pose organisational and maintenance problems on the long run, as well as problems to transfer the ground. Natural and stimulated attenuation seem very attractive, but we have to be very careful. A consultant has to prove that he knows well enough all relevant soil parameters and that he can model decently what will happen in the future. Monitoring of attenuation is not always evident and may prove to be rather expensive in the long run. Most in-situ concepts offer not a complete remediation of a site; on the long run, we have to take into account that when the use of the ground changes, the contamination may pose serious risks again and that the future use may be hindered.

5. PRESENTATION VISUALS ~ presented by Victor Dries

In-situ treatment: deus ex machina or jack-in-the-box?

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Slide 10/20/04

Impact legislation

- New contamination:
Immediate remediation when > SRS
SRS depend on soil use
- Historical contamination
remediation when risk
at moment transfer or after priority

Slide 11/20/04

Impact legislation (2)

- Remediation goal: BATNEEC
 - If possible: background level
 - If not possible: < SRS
 - If not possible: no risk

Slide 12/20/04

In-situ treatment

- Pump and treat is well accepted
 - offers little guarantee
 - often used with too little study
 - recalcitrant contaminations take very long
- Soil venting (and bioventing) is quite popular and well accepted
- Air sparging is growing and quite well accepted

Slide 13/20/04

Soil investigation

- Investigation problems:
 - samples give limited information (hor. + vert.)
 - good information of contamination implies either a lot of money or a lot of time
- Alternatives:
alternative detection + analysis methods
watch out for on-field validation

Slide 14/20/04

Soil investigation

- Laboratories
 - very little quality assurance
 - value of accreditation systems?
 - round robin for accreditation

Slide 15/20/04

Recoveries of dichloromethane in soil

126.0%	93.2%	92.6%	110.7%	72.6%
117.1%	134.6%	88.9%	110.6%	84.1%
7.5%	108.6%	124.3%	80.0%	102.2%
101.4%	84.6%	81.2%	159.2%	89.4%
88.5%	100.6%	107.8%	78.0%	104.6%
88.7%				

Slide 16/20/04

Natural attenuation

- many data needed: expensive invest
- difficult modelling
- monitoring: long + difficult
- laboratory results
- neighbours are often very near

Slide 17/20/04

Natural attenuation (2)

- "Enhanced" attenuation
 - source removal
 - in-situ treatment
- ♥ part of contamination is removed
- ♥ faster
- ♦ good modelling + monitoring



Video 0001/001M

Slide 11

Source boosting

- Mobilisation of recalcitrant contaminations
- Reduces time frame P&T strongly
- Almost unknown in Europe so far
- ♦ Hydraulic control of mobilised contamination



Video 0001/001M

Slide 12

Containment

- Hydrogeological containment used on waste dumps in use
- Containment walls and "wrap and dump" quite popular for big problems
- Active walls coming, not easily accepted
- Immobilisation in active study



Video 0001/001M

Slide 13

Containment (2)

- ♦ nothing has eternal life: semi-natural concepts vs liners
- ♦ contamination stays present
- ♥ active walls
- ♦ duty of care + maintenance
- ♦ future use
- ♦ monitoring: self-controlling system?



Video 0001/001M

Slide 14

Conclusions

- Reliability of lab analyses?
- Good modelling is necessary
- Good monitoring is expensive and hard
- Maintenance is important
- Isolation and attenuation may impact future use + transfer price



Video 0001/001M

Slide 15

Know what you do,

do it well and

keep on doing it



Video 0001/001M

Slide 16

NEEDS, VIEWS, AND CONCERNS OF THE SITE OWNERS

Terry Walden¹

1. ABSTRACT

In-situ remedial systems generally fall into two category types. The first is a *Stationary* system that involves the use of installed wells (or trenches) for moving air or other remedial fluid through the formation. In these systems the soil is left relatively undisturbed. The second system is a *Disruptive* system where the soil is physically disturbed to achieve treatment. Examples here include landfarming or in-situ soil mixing with large augers.

Remedial performance validation is dependent on the type of system employed. Sentinel wells at the downgradient boundary and within the footprint of the treatment area are normally used for a Stationary system, where the goal is for all (or at least 95%) of the sentinel wells to meet a risk-based clean-up concentration. In a Disruptive system, it is typical to place a regular grid pattern over the area following treatment and take samples at each node to verify that the target has been achieved. The grid is sized so that any untreated - or less than satisfactorily treated - area has a radius less than a specified maximum.

While conceptually it would be appealing to perform grid-based verification on all remedial systems, site owners would be very reluctant to agree to this approach on Stationary system designs. Experience has shown that such systems typically take longer than specified - and may require additional infill wells - to achieve the promised goals, or may never achieve the objective within a satisfactory time frame. Even more fundamentally, the heterogeneous nature of an undisturbed soil media almost guarantees that some zones will be bypassed, typically those having a lower permeability where contamination may be concentrated. So having typically spent additional money and time to achieve a clean-up target on the sentinel wells, site owners would be leery of sampling additional locations where one exceedence could delay a real estate transfer (even though it may little impact on overall risk). If a gridded validation were specified by the regulator at the time the system decision is taken, it could well result in selection of a more predictable ex-situ remedial design.

2. INTRODUCTION

This paper expresses the perspective of the site owner with regard to the validation of in-situ remediation performance. The site owner view in this case is the oil company, BP, and the experience shared is BP's European practice on the topic. The experiences discussed are not to suggest that these are BP's policies, but simply the approach that is commonly taken at BP's retail stations, terminals, lube plants and refineries in Europe.

3. BP'S PRESENCE IN EUROPE

BP has operating sites or plants in 10 countries in Western Europe, including the UK, France, Benelux, Germany, Austria, Switzerland, Spain, Portugal, Greece and Turkey. In addition there are a few countries, like the Scandinavian countries and Italy, with a lubricant presence due to the recent acquisition of Castrol. In-situ remediation systems have been installed in most of these countries over the past several years. Primarily these consist of soil vapor extraction systems for treating soils in the vadose zone, and air sparging systems for in-situ treatment of groundwater. In addition, in-situ systems for free product removal include dual or multi-phase extraction using a high vacuum blower.

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4. REMEDIAL GOALS

Other than in jurisdictions where it is prohibited, remedial goals in BP are generally determined on a risk basis. There are actually few (or no) countries in Europe where a risk approach is explicitly stated as unacceptable, although there are always local regulators to whom the process may need to be demonstrated and validated before getting their approval.

Remedial goals generally start with a requirement to remove a certain amount of – perhaps all – the free product in wells. The treatment endpoint in this case is a thickness of product not to be exceeded in one or more wells across different seasons. Note that free product usually manifests itself to the greatest extent in the dry season when water tables are low.

Human health or ecological risk goals generally require achievement of a soil and/or groundwater concentration that meets acceptable risk criteria. So the overall remedial goals at a site are generally to leave no more than a minimum thickness of free product in certain or all recovery wells, and to achieve a soil/groundwater concentration protective of human health and the environment.

5. SYSTEM CLASSIFICATION

For purposes of validating performance, in-situ systems can basically be broken down into two types:

- a. Stationary Systems: By this is meant that the soil is left relatively undisturbed by the remedial system, with only wells (or perhaps trenches) installed for in-situ treatment. Examples are soil vapor extraction, air sparging or multiphase extraction wells.
- b. Disruptive Systems: In this case the soil is disturbed in order to treat it. In-situ examples include landfarming (where the surface soil is tilled to facilitate bioremediation) and soil mixing (use of large augers to mix biological or chemical reagents with the soil or to stabilize it by introducing a cementing mixture).

6. REMEDIAL VALIDATION PRACTICE

From a site owner perspective, the method of validating remedial performance is a function of the type of system installed:

- a. Stationary Systems: It is preferred to have a series of sentinel wells identified for achievement of the remedial target concentration. These wells are typically not the vapor extraction or sparge wells, as these wells would receive preferential treatment by virtue of being part of the remedial design. The sentinel wells are normally located at both the downgradient boundary of the site and within the footprint of the treatment area. The layout of the wells within the footprint should be such that achievement of the target at their locations assures overall treatment of the whole of the remedial area.
- b. Disruptive Systems: When the soil has been disturbed for treatment, the preferred validation approach is to *grid the site* for validation monitoring. The grid is normally a square or rectangular pattern with a spacing appropriate for ensuring that any inadvertently untreated, or less than satisfactorily treated, source zone has a radius less than a specified maximum. Again the targets to achieve are generally risk-based concentrations.

7. CONCLUSIONS AND DISCUSSION

The use of sentinel wells for stationary systems and a validation grid for disruptive systems seems fairly straightforward. A good question to ask however is why a validation grid is not used for all in-situ systems, regardless of type.

Site owners would not be happy to have a validation grid for stationary systems. One hidden message here concerns the lack of confidence in stationary in-situ systems. This is especially true in countries which have traditionally conservative standards, such as Germany or the Netherlands, where meeting a target is difficult. In some cases the systems have not been able to achieve the promised remediation target within the scheduled time frame and often, additional treatment wells must be installed to reach areas or locations in the soil column where the air does not appear to travel. In certain circumstances, the systems have been abandoned in favor of a *dig and dump* scheme at significant cost while also delaying a potential real estate transfer date.

There may be plausible reasons for the shortcomings of the in-situ system. Perhaps it was ill suited for the geology or contaminant type. Perhaps the design was flawed with too large a spacing between wells. But more importantly, it is probably unrealistic and asking too much of a system to achieve very detailed clean-up over a wide area in a media (soil) where there are natural heterogeneities, such as low permeability strata. These anomalies can trap contamination and are un-amenable to treatment by air-based systems where the flow may bypass them.

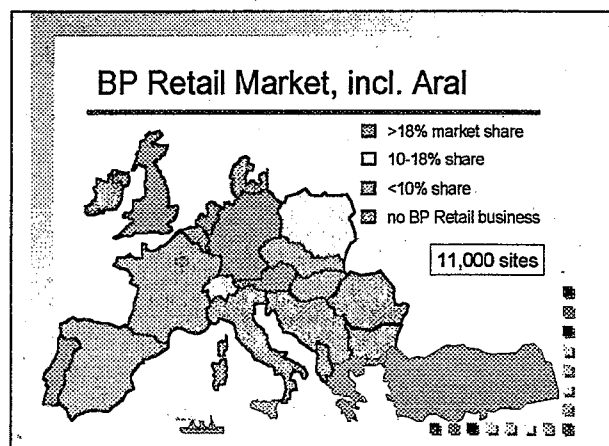
Having normally spent additional time and money to achieve a risk-based concentration target at all the sentinel wells, operators would be very reluctant to open the site up to gridded monitoring from new well locations. The likelihood is too high that lower permeability untreated zones may be encountered, thus further delaying the closure or sale date, even though concentration exceedences at a few wells would likely have a negligible impact on the overall human health or ecological risk. If a gridded requirement were specified by the regulatory authorities in advance of the decision on the remedial system, it could likely change the outcome in favor of an ex-situ disruptive system, such as composting or thermal desorption.

8. PRESENTATION VISUALS ~ presented by Terry Walden

NATO Special Session

Validation of In-Situ Remediation
- Site Owner Perspective -

Terry Walden
BP Oil - London
September, 2001



Common Remedial Goals

1. Free product removal to minimum thickness

2. Soil & groundwater concentration targets protective of human health & environment

In-Situ Remedial Systems

Stationary Systems → soil left undisturbed

- Soil vapor extraction wells or trenches
- Air sparge wells
- Chemical flush wells

In-Situ Remedial Systems

Disruptive Systems → soil is disturbed

- Landfarming
- Soil mixing with large augurs

Stationary System Validation

Sentinel Wells

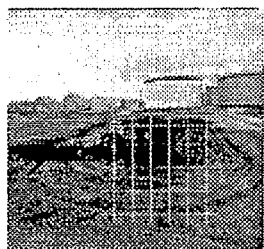
- Downgradient boundary ▲
- Within footprint of treatment area ●

Netherlands Terminal: Target of 1 ug/l benzene - all wells

Disruptive System Validation

Grid Monitoring

- ❑ Square or rectangular grid
- ❑ Sampling at nodal points



Why Not Grid Monitoring Everywhere

- ❑ Experience with Stationary Systems in Europe
 - ◆ Generally take more time and money to achieve clean-up goals
- ❑ Inherent Limitations of Stationary Systems
 - ◆ Heterogeneities in soil (esp. lower permeability media) may be unavailable to air flow
- ❑ Difficulty with One 'Hit' Above Target
 - ◆ Regulatory impasse, even though it may have little impact on overall risk

Conclusions

- ❑ Current validation protocol is 'fit for purpose'
 - ◆ Sentinel wells for well-based remedial systems
 - ◆ Grid monitoring when soil media fully disturbed
- ❑ Complete 3-D clean-up with Stationary systems unrealistic, but
 - ◆ Impact on overall risk from one 'hit' small
 - ◆ Natural attenuation likely to take care of problem
- ❑ Imposing grid monitoring everywhere could result in more use of ex-situ technologies or 'dig and dump'

NEEDS, VIEWS, AND CONCERNS OF THE INSURANCE COMPANIES

Dominique Ranson¹

1. SUMMARY

Investigating and redeveloping contaminated property used to have more risks than benefits. The potential for environmental liability or unknown cleanup costs often turned an attractive real estate deal into a financial nightmare.

Environmental insurance has made investment in contaminated property less risky over the past decade. The insurance industry has found solutions for environmental uncertainties by offering pollution insurance for known, as well as unknown environmental liabilities.

A site cleanup project for known environmental liabilities represents, in general, one of the most important environmental liability exposures. Insurers have developed their own specific way to assess the insurability of a clean-up program via a review of the remedial action plan, contemplation of containment of the cleanup costs within the insurance program, and inclusion of unknown as well as known pollution conditions in an environmental insurance program. Environmental insurance now permits optimization of internal risk management capabilities and prevents the break down of property transfer negotiations due to uncertainty associated with known or unknown environmental liabilities. Conclusions will be illustrated during the lecture with claims scenarios and cases in which insurance solutions facilitate property transactions.

2. KNOWN VERSUS UNKNOWN POLLUTION CONDITIONS

A property owner can protect himself against unforeseen and unexpected cleanup costs that are above the anticipated cost for a cleanup project by purchasing Cleanup Cost Cap insurance. These known pollution conditions are always within the self-insured retention and the Cleanup Cost Cap insurance is excess of this self-insured retention.

Pollution conditions may also be unknown because there is no relevant data on the historic use of the property, the pollution or its consequences (cleanup, bodily injury, property damage) have never manifested, or current legal obligations or orders by the authorities may significantly change. These types of environmental liabilities may be insurable as unknown pollution conditions.

3. POLLUTION AND ENVIRONMENTAL LIABILITIES

Polluted sites often result in third party liabilities. These preexisting conditions resulting from historic site operations or gradual releases typically are not insured within the classical general liability insurance program in Europe, with a limited exception for Germany, where certain types of facilities have the obligation to buy coverage for third party liability related to pollution conditions (UHV). However, on-site cleanup costs are almost in every case not insured and even excluded. Policy wordings must be carefully reviewed, particularly when more than one policy is in place: Not only "known" versus "unknown" but also origin, causality, sudden & accidental versus gradual coverage, primary versus excess (UHK- lower retention/ deductibles under one policy versus another) as well as historical pollution issues may become serious sources of discussion in a claim situation when more than one policy is involved.

¹ Environmental Insurance Manager AIG Europe. Kortenberglann 170-B-1000 Brussel

Clean up of soil and groundwater is generally expensive, can be unpredictable and can turn into a financial nightmare. In some European regions, soil and groundwater contamination already jeopardize property transfers and lease and rental agreements.

In order to be able to provide insurance, the insurance industry has techniques to assess the likelihood of occurrence of unknown environmental liabilities and the uncertainty related to environmental cleanup. The likelihood of occurrence of unknown environmental liabilities is essentially assessed by examination of the underwriting information. This underwriting information consists essentially of detailed data regarding site history, dangerous goods and waste storage management, dangerous goods processing and transport, environmental compliance and management, security, hydrogeological characteristics, air and surface water emissions and sensitivity of the neighborhood.

4. MOST IMPORTANT UNCERTAINTY FACTORS RELATED TO ENVIRONMENTAL LIABILITIES

4.1 Site Related Factors

One of the most important site related factors in the site history. During the environmental underwriting process the site history is assessed in detail because it contains relevant information with regard to the potential presence or absence of different types of pollutants resulting from improper waste handling (buried waste), gradual releases over the facilities operating history, effluent discharges, etc... The site history may also explain the presence of third party liabilities or other outside influences. In some cases due diligence audits or phase I environmental audits contain sufficient site history information. Sometimes more investigation may be required by the underwriter to fill gaps prior to underwriting the exposure. Some site related factors are site or facility specific. Those features are essentially related to the local environment (such as use of land, surrounding land use, presence of drinking water wells, natural resources (lakes, rivers, streams...), the general exposure to third parties related to the pollution and the extent of the contaminants.

Especially with regard to cleanup cost potential, knowledge of surface soil and groundwater characteristics is essential. In most of the European region the environmental authorities require risk-based assessments in relation to the necessity and efficiency of cleanup. Factors such as permeability, transitivity, depth of groundwater table and ground water vulnerability, clay/organic matter content, presence of ground water wells and their application, hydrogeologic characterization...are typical data required for the environmental underwriting process.

Sites under exploitation on which environmental cleanup occurs or will occur need specific attention with regard to the management of the site. In general, environmental management, dangerous goods storage and distribution, waste handling and storage, are important risk factors and may cause additional pollution conditions or complications during cleanup. Also of vital importance is the accessibility to third parties and the way construction and remediation are implemented by the contractor.

4.2 External and Other Factors

Environmental underwriting requires a good understanding of the expertise and experience of the environmental consultant working for the insured as remedial expert. One of the basic requirements is the presence of a multi disciplinary team working within the environmental consulting organization, as site assessments and remedial design require such a multi disciplinary approach. The ongoing exponential development of new remedial technologies requires sufficient up-to-date know-how of the environmental designer. Especially in those regions where the local authorities are part of the cleanup project, the environmental Consultant Company must be able to provide local specialized employees able to negotiate with local authorities or other official bodies.

In order to be able to assess the comprehensiveness of the remedial budget (or self-insured retention), the level of investigation performed is elemental.

The most important factors are:

- Degree of reliability of the laboratory results
- Geostatistical criteria related to the sampling of soil and ground water
- The sampling procedures and representativeness of the analyzed samples
- Degree of reliability of site history analysis, data on subsurface soil and ground water characteristics, site features and analysis of the extent of the contamination.

In many cases, environmental law, future use of the property, surrounding environment, exposure to public and the environment, will influence the way in which cleanup has to be performed.

Depending on the attitude of the public towards the facility of the insured (and its eventual contamination) the requirements of the degree of cleanup could become completely different from that expected in a "normal" or similar situation elsewhere. It is therefore crucial to be aware of any known or reported claims, pending claims, consent orders, prosecutions, against the insured. Public perception generally does not influence the obligation to cleanup (which is based upon environmental law). Public perception will however push the insured to be more compliant and environmentally conscious.

Unexpected clean up costs are in many cases related to the (sometimes) unpredictable conduct of the pollutants, unknown historic uses of the property, surrounding operations, or poor delineation. Knowledge, therefore, regarding hydrogeological conditions and hydrodynamic behavior of the pollutants, historic uses of the property and proper investigations are essential. Because in many regions the environmental authorities apply a risk based approach, it is also essential to understand the biological attenuation and the toxicology (including the availability) of the pollutant.

Environmental authorities are a significant party within the remedial cleanup process. Their attitude influences the way cleanup will be performed and their likelihood of changing their orders. The political factors, sensitivity of the authorities towards pollution and the legal frame are criteria of consideration during the environmental underwriting process.

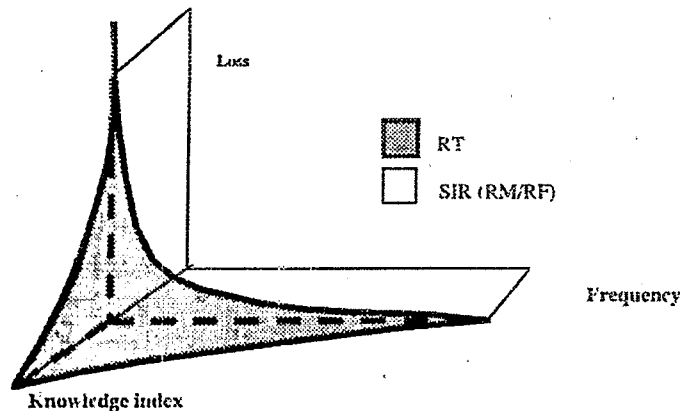
5. INSURABILITY OF ENVIRONMENTAL (SITE) CLEANUP

5.1 How are Environmental Risks Dealt with in Terms of Underwriting?

Environmental insurers rely primarily on their own evaluation and assessment of the factors stated above rather than on insurance industry loss statistics.

Many property and general liability losses with environmental causalities are generally not reported as environmental losses. One of the most important distinctions to be made is the difference between known and unknown pollution conditions, as there is generally no possibility to insure known losses, above environmental law, on a risk transfer basis.

Figure 1: Loss -, frequency and knowledge indices determine the field in which environmental insurers are willing to participate in the risk (RT or risk transfer section). Outside this delineated field, whereof shape and extent is on a case-by-case level, the risk/loss is within the SIR.



For known pollution conditions however, there are possibilities to insure in excess of the self-insured retention (SIR). This self-insured retention level also depends on the know-how on existing pollution conditions and environmental care (Figure 1).

Statistical know-how based upon experience with similar cleanup projects, loss history analysis of the site, and knowledge of privileged partners (external and own consultants – in the case of AIG, AIG Consultants, Ltd.) gives the insurer the ability to offer environmental insurance solutions. Other extremely important consideration criteria in the underwriting process are the results of the detailed analysis of the remedial action plan and the financial strength of the insured. In-house environmental underwriting experts do environmental underwriting at AIG.

5.2 Environmental Insurance Solutions

In the case of presence of known conditions on which a cleanup is legally required, the insurance industry is able to provide coverage for the costs in excess of the SIR. This insurance solution is called: Cleanup Cost Cap insurance.

Unknown pollution conditions and third party liabilities are generally covered by site-specific environmental insurance policies, such as the Pollution Legal Liability policy, perfectly fitting between property and liability insurance policies. Especially in those cases in which property transactions occur, brownfields are developed, multiple year coverage is necessary or balance sheets protections are required, blended insurance programs (such as the environmental protection program) provide tailor made solutions.

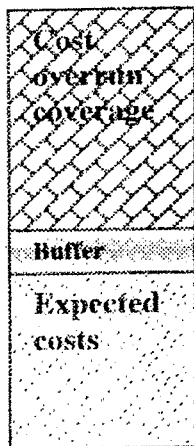
6. CLEANUP COST CAP PROGRAM

The Cleanup Cost Cap policy indemnifies the insured for cleanup costs, as defined in the remedial study, that are above the anticipated budget for cleanup of the site or facility. The policy offers coverage for cleanup costs at, adjacent to, or from a defined site location. The coverage consists of an attachment over the SIR, which is generally equal to the expected costs of cleanup plus a buffer layer (Figure 2). For the known pollutants, there's coverage provided in the event:

- The actual contamination is greater than estimated
- Off site cleanup is required adjacent to the covered site
- Off site cleanup due to emanation of the pollution from covered site
- Governmental authorities change orders in course of the cleanup project

The policy covers the remedial action plan, becoming a part of the policy and describing exactly the area in which environmental cleanup occurs. The Cleanup Cost Cap also offers an option covering newfound contamination while conducting the cleanup. This option also includes coverage for cleanup in case off-site contamination from those newfound pollutants occurs from the covered location.

Figure 2: Basic insurance structure of the cleanup cost cap program: The SIR is equal to the expected costs of cleanup plus a buffer layer. Above this SIR there is a cost overrun coverage (a "cap" or excess of loss). Premium discounts are available in case the insured participates in the excess of loss section.
Numerical example: SIR= 2,240,000 Euro; cost overrun coverage= 3,760,000 Euro



The information required to underwriting a Cleanup Cost Cap policy includes the environmental site assessments (phase I, II, risk assessments (REBECCA, C-SOIL, Volasoil etc.), hydrogeological assessments, etc.), the remedial action plan (including different cleanup alternatives and budget estimates) and the eventual agreement with the contractor who will execute the remedial work.

The Cleanup Cost Cap (CCC) properties at AIG are:

- 100,000,000 US\$ available per site
- Multi-site programs can be offered
- In suitable for blended insurance solutions
- Terms up to 10 years available.

7. POLLUTION LEGAL LIABILITY

AIG's Pollution Legal Liability policy (PLL Select) generally provides coverage for operations facilities. The coverage includes on-site and off-site cleanup from pre-existing and new pollution conditions, on-site and off-site third party bodily injury as well as on-site and off-site third property damage due to pollution conditions. The insurance program can be tailor made (different basic coverage options) depending on the risk-management needs of the (insured). In addition to the insurance program, PLL Select offers coverage for business interruption and transportation to and/or from a covered location. There's generally no distinction made between sudden or gradual pollution, because in many claims scenarios it is almost

impossible to differentiate between the two. The policy trigger of PLL Select is the legal obligation to carry out environmental cleanup. Coverage is provided for owned, leased or rented sites.

The PLL policy doesn't provide coverage for existing contamination (this is done by the Cleanup Cost Cap policy), but provides coverage during the policy term in case pollution conditions arise, which is not covered under new found conditions in the Cleanup Cost Cap policy, a cleanup is required. PLL can be combined with a CCC program or can be purchased after execution of the remedial work.

8. BLENDED INSURANCE: ENVIRONMENTAL PROTECTION PROGRAM

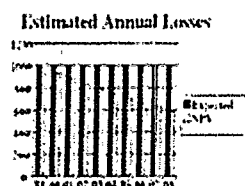
By means of example of blended insurance solutions, the Environmental Protection Program (EPP) gives the ability to combine numerous advantages related to environmental insurance:

- The policy creates a well defined scope of action
- There is an excess coverage provided
- Expected costs are discounted
- Rewards are provided in case of favorable loss experience
- Provides high guarantees in case of property transaction
- Protects budgets and balance sheets

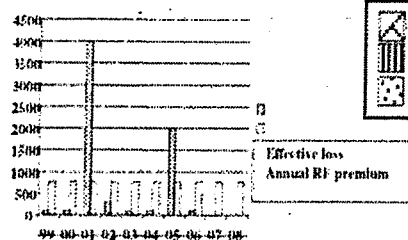
The Environmental Protection Program is, technically speaking, a combination of a finite risk insurance construction (RF) and an excess of loss coverage (Figure 3). For example, a known condition might require environmental cleanup and is associated with a budget of 10,000,000 US\$. The legal obligation to execute cleanup may be expected within the first 10 forthcoming years. The known potential loss is ventilated over this period, resulting in a net present value (NPV) over the amount of years. The average NPV is a criterion to determine the RF premium. In addition to the RF section, the insurer provides an excess of loss coverage.

Figure 3: Environmental Protection Program construction

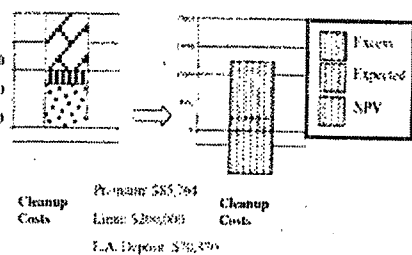
How does it work?



How does it work? (2)



How does it work? (3)



9. CLAIMS SCENARIOS

By investigating the different claims, which have occurred within the industry, as presented during the lecture, the most frequent causalities of losses are due to the discovery of additional or new soil contamination. In a lot of cases additional costs arise due to accessibility problems for excavation, difficulties in site geology and greater ground water contamination extensions. Other cases of loss are related to inadequate soil and ground water sampling, under-estimation of laboratory and consulting costs and insufficient defined actions to be taken within the Remedial Action Plan (RAP).

Many claims are also associated with discovery presence of unknown pollutants during the execution of the environmental cleanup (such as asbestos, pesticides, PCB's, etc). Claims vary between 20-300% of the SIR.

10. CONCLUSION

Environmental underwriting can not be compared with the daily way of underwriting risks in the insurance industry. It requires a detailed assessment of all kinds of factors that might influence the extent and scale of known and unknown pollutants. Environmental liability exposures, whether known or unknown, can jeopardize property transactions, as they are normally insufficiently insured or not insured at all within the general liability or property insurance programs (the classical insurance). Environmental insurance is the adequate answer to situations in which financial guarantees are required to cover environmental liabilities. Environmental insurance and blended insurance programs are oftentimes purchased in cases of mergers and acquisitions and brownfield development situations. Contractors are also interested to offer coverage for cost overrun due to environmental cleanup. Insuring the environmental liability might create financial advantages such as off-balance sheet and budgetary protection.

11. PRESENTATION VISUALS ~ presented by Dominique Ranson

Needs and criteria for the insurance

Dominique Ranson
Manager Environmental Insurance
AIG Europe

Program

- Insurance: basic principles
- Environmental liabilities.
 - known or unknown
 - cleanup required or not?
- Insurability of environmental (site) cleanup and liabilities?
- Solution:
 - cleanup cost cap
 - Blended insurance: EPP
 - PLL
- Claims scenario's

Insurance: basic principles

- Insurance = financial protection against losses with unforeseen character
- Classic Insurance: unforeseen equals sudden and accidental
- Casualty: insurance for third party losses (general liability)
- Property: first party coverage (own property, premises, ...): fire insurance, boiler & machinery, ...

Environmental Insurance

Property	Environmental	General liability
<ul style="list-style-type: none"> Fire Explosion Boiler & machinery Business interruption Flood Storm 	<ul style="list-style-type: none"> Dead Pre-existing 2000 5 & 10 	

Environmental liabilities

Known or unknown pollution

- Polluted sites can result in third party liabilities
- The cleanup of soil and ground water is generally expensive, sometimes unpredictable
- In some European regions, soil and ground water contamination jeopardize property transfers
- Site history, dangerous goods and waste storage, dangerous goods processing and transport are very important
- Lease and rental agreements

Most important uncertainty factors related to cleanup


- Site related factors
 - Site history
 - subsurface soil and ground water characteristics
- Site management
- other site features

Most important uncertainty factors related to cleanup (2)

- External, other factors
 - experience and expertise of environmental consultant
 - level of investigation performed
 - public perception
 - conduct of the pollutants
 - attitude of the authorities


Site history

- Part of the site characterization is the site history. In some cases the site history is insufficient documented in phase I studies
- The site history explains the potential presence or absence of different types of pollutants or buried waste
- It also may explain the presence of third party liabilities or outside influences




subsurface soil and groundwater characteristics

- ▼ Permeability
- ▼ Transmissivity
- ▼ depth of groundwater table
- ▼ vulnerability of the ground water
- ▼ clay/organic matter content
- ▼ ground water wells
- ▼ ...




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Site Management

- ▼ Environmental management
- ▼ Accessibility for third parties
- ▼ Dangerous goods storage and distribution
- ▼ Waste handling and storage
- ▼ Construction works
- ▼ ...




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Other site features

- ▼ Typical examples are the presence of buried waste of chemicals (barrels).
- ▼ Other features are:
 - local environment (use of land, presence of drinking water wells, ...)
 - general exposure related to the pollution
 - extend of the contamination
 - ...




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Experience and expertise of environmental consultant

- ▼ Site assessment and remedial design requires a multi disciplinary approach
- ▼ Exponential development of soil and ground water cleanup technologies require sufficient up-to-date know how
- ▼ Local presence (especially in cases in which negotiations with local authorities are required) is essential




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Level of investigation performed

- ▼ Degree of reliability of laboratory results
- ▼ Geostatistical criteria
- ▼ Sampling procedures
- ▼ Degree of reliability of
 - Site history analysis
 - subsurface soil and ground water characteristics
 - site features
 - analysis of the extend of contamination




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Public perception

- ▼ What's the attitude of the public with relation to the facility (and eventual existing contamination)
- ▼ Any known or reported claims, pending claims, consent orders, prosecutions.




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conduct of the pollutants

- ▼ Hydrological conditions and hydrodynamic behavior of pollutant is an essential knowledge in order to predict the possible conduct of the pollutants (in future and during cleanup)
- ▼ as environmental authorities apply more and more a risk based approach it is essential to understand the biological attenuation and the toxicology (including availability) of the pollutant
- ▼ toxicology




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Attitude of the authorities

- ▼ Political factor is very important
- ▼ Sensitivity to the pollution
- ▼ There is a significant evolution towards a risk based approach in most of the European countries
- ▼ legal frame
- ▼ likelihood of changing orders




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Insurability of environmental (site) cleanup

- ▼ How is dealt with environmental risks in terms of underwriting?
- ▼ What are the environmental insurance solutions?
 - Clean-up Cost Cap
 - Environmental Protection Program
 - Pollution Legal Liability




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How is dealt with environmental risks in terms of underwriting?

A. General

- ▼ Environmental underwriting (third party liability and cleanup cost) only relies to a very small part on statistics
- ▼ All potential items/factors as stated above need to be investigated




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How is dealt with environmental risks in terms of underwriting? (2)

B. Known pollution conditions

- ▼ Statistical know how is essential based upon experience with similar projects, loss histories and knowledge of our dedicated consultants (AIG Consultants Ltd.)
- ▼ Detailed analysis of remedial action plan
- ▼ Financial strength of the insured




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How is dealt with environmental risks in terms of underwriting? (3)

C. Unknown conditions and liabilities

- ▼ Relevant and sufficient underwriting information is necessary.
- ▼ SIR-level depending on know-how on existing pollution conditions & environmental care
- ▼ Underwriting is done by environmental experts




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What are the environmental insurance solutions?

- ▼ Known conditions and cleanup required: **Clean-up Cost Cap**
- ▼ Unknown conditions and third party liability: **Pollution Legal Liability**
- ▼ Blended insurance solutions: **Environmental Protection Program**




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Cleanup Cost Cap

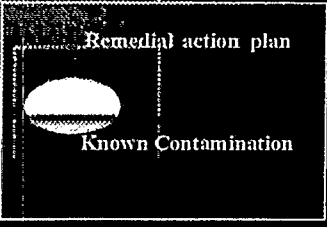
- ▼ Indemnifies the insured for cleanup costs, as defined in the remedial study, that are above the anticipated cost of cleanup.
- ▼ Coverage is provided for cleanup costs at, adjacent to, or from the defined site location.
- ▼ The policy attaches over a prescribed self-insured retention, (SIR), which is generally equal to the expected cost of cleanup plus a buffer layer.




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How does it work?



The diagram illustrates the relationship between the site boundary, the remedial action plan, and the known contamination. A rectangular box labeled 'Site Boundary' contains a smaller rectangular box labeled 'Remedial action plan'. Inside the 'Remedial action plan' box is an oval labeled 'Known Contamination'.




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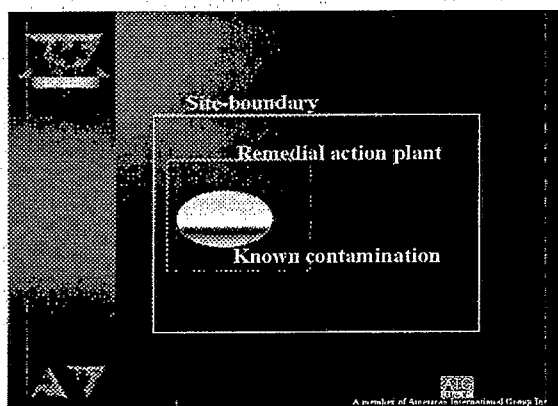
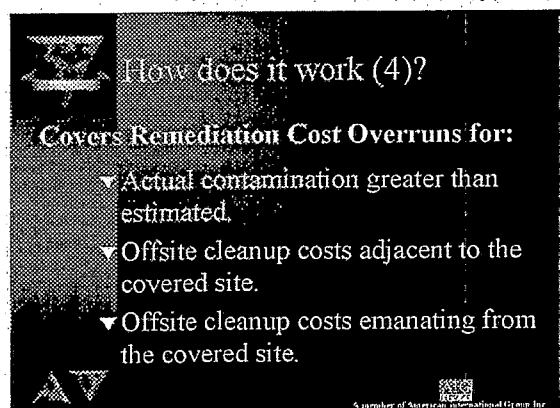
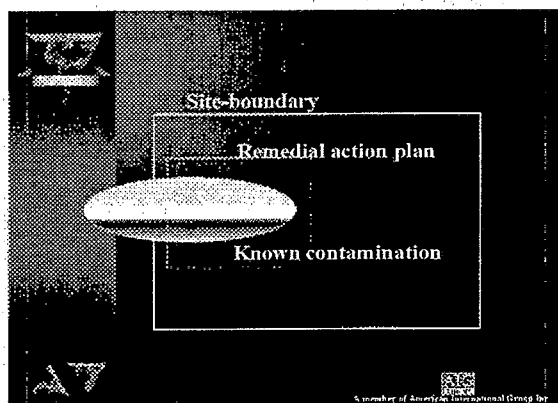
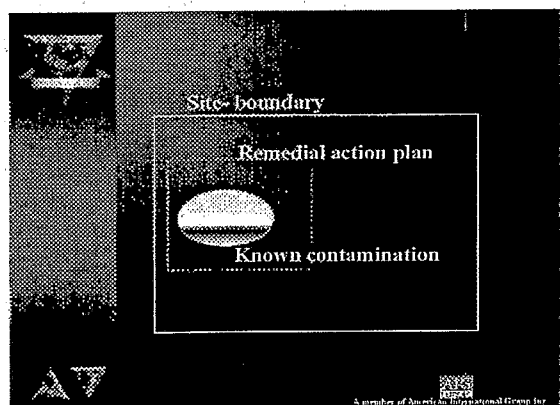
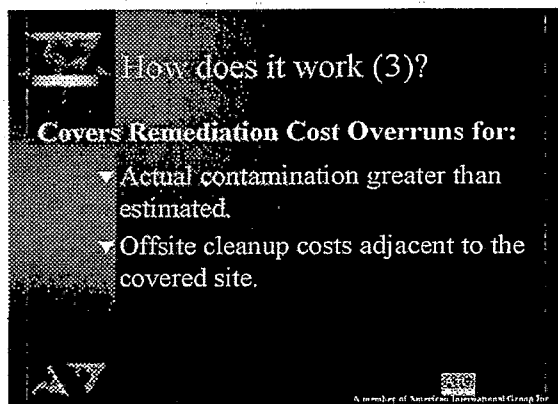
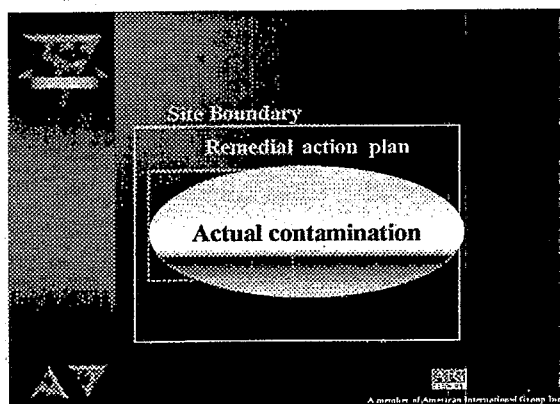
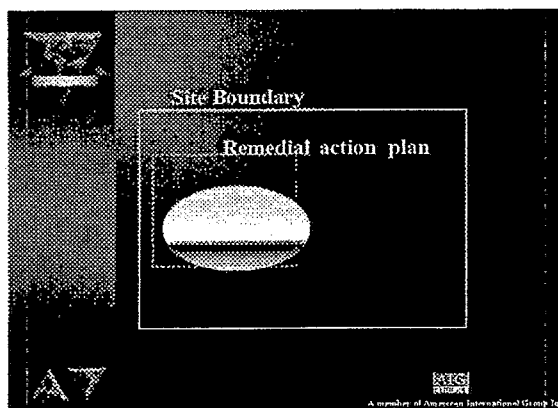
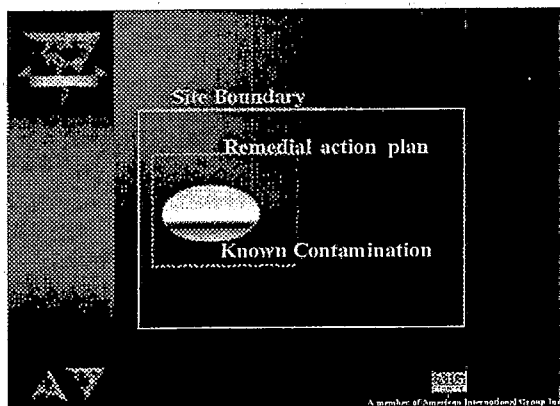
How does it work (2)?

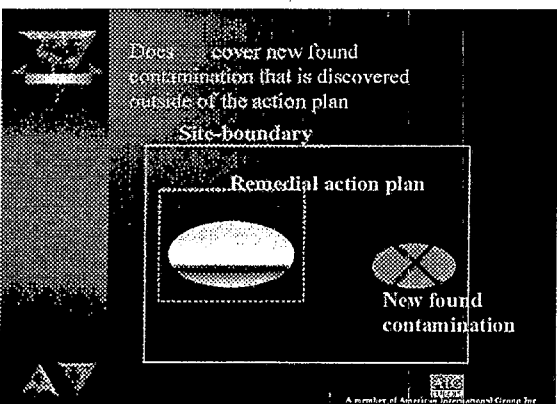
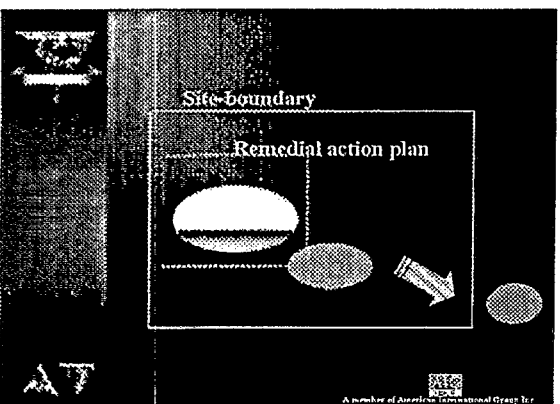
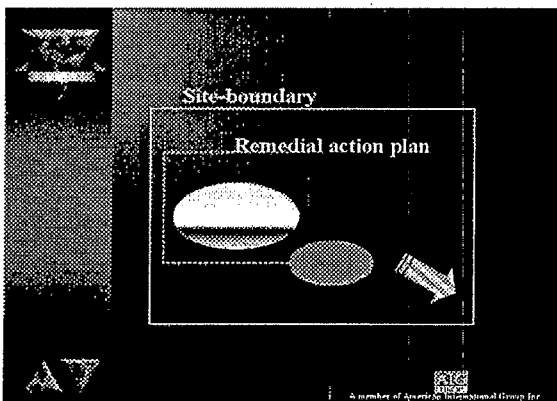
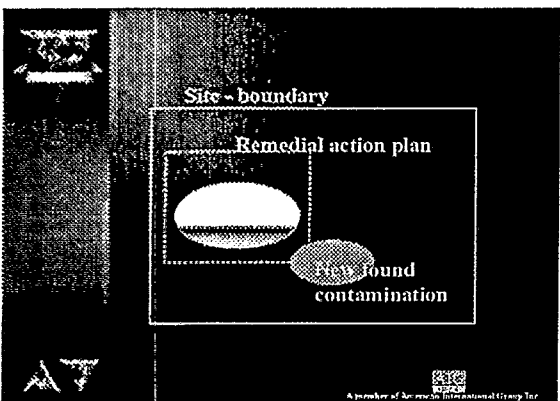
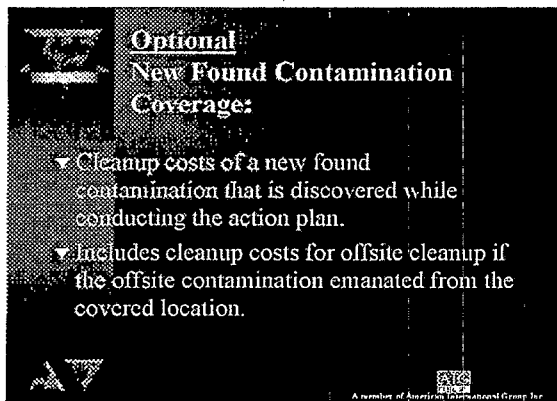
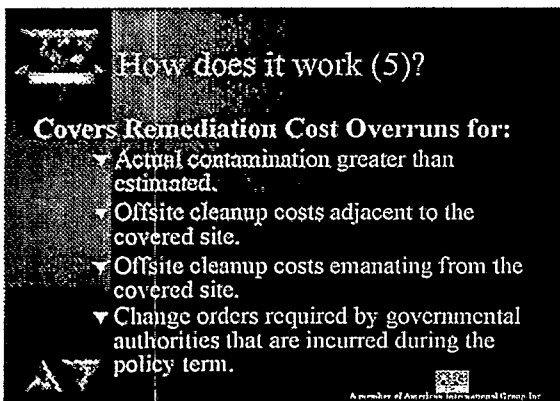
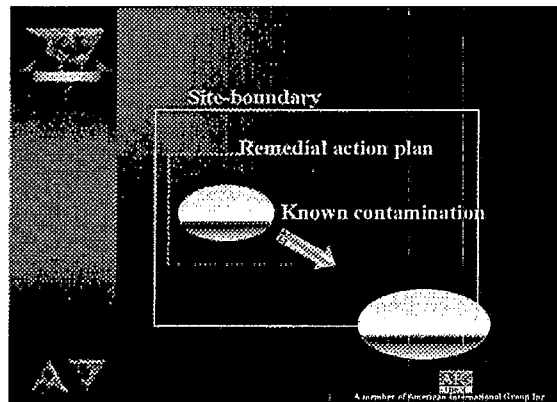
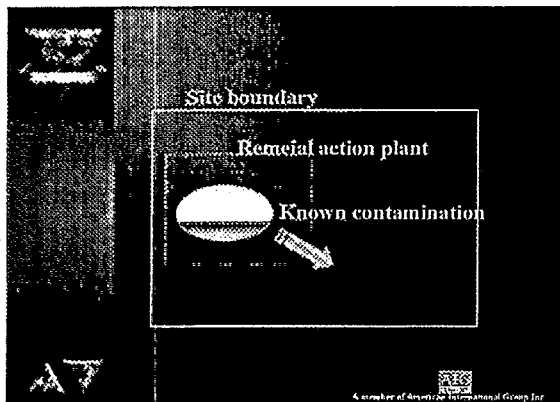
Covers Remediation Cost Overruns for:

- ▼ Actual contamination greater than estimated.



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Basic Structure:

- ▼ Coverage attaches above the expected clean up.
- ▼ Premium discounts are available if the insured elects to have the coverage attach excess of a buffer layer.

Cost
overrun
coverage

Buffer

Alternative structure

- ▼ Co-insurance or risk participation (contractors, third parties, insured) in stop loss layer

Cost
overrun
coverage

Buffer

Properties

- ▼ 100 Mio € per site limits available.
- ▼ Multi-site programs can be offered.
- ▼ Blended insurance possibilities
- ▼ Terms of up to ten years available.

Underwriting information



- ▼ Environmental site assessment reports (phase I, II, risk assessment, hydrogeological assessment. ...)
- ▼ Remedial action plans
- ▼ Contractor's agreement
- ▼ Mergers/acquisition agreement

Benefits

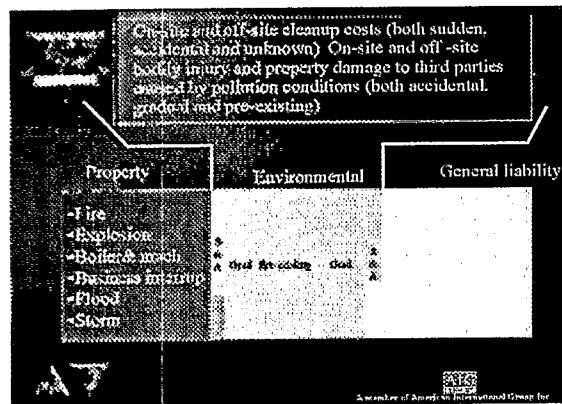
- Helps assure that funds will be available for entire cleanup of contaminated site
- Protects against financial loss that could inhibit owners' operations and profitability
- Satisfactory to a lending institution, which may be fearful of incurring liability or losing the value of the loan
- Property can be put back to productive use while protecting human health and the environment

Unknown conditions: Pollution Legal Liability (PLL)

- ▼ Coverage for sites in exploitation
- ▼ Coverage includes the following:
 - On-site and Off-site cleanup costs from pre-existing and new pollution conditions
 - On-site and off-site third party bodily injury
 - On-site and off-site third party property damage
 - Transportation to and/or from the location
 - Business Interruption

PLL (2)

- ▼ PLL doesn't cover remedial plans (such as CCC) but provides coverage during the policy term in case a remediation needs to be done (for new, gradual or pre-existing conditions)
- ▼ It fits perfect between property and liability policies and optimizes the risk management
- ▼ It can be combined with a CCC program or is purchased after cleanup
- ▼ Responds to "gaps" in classical insurance

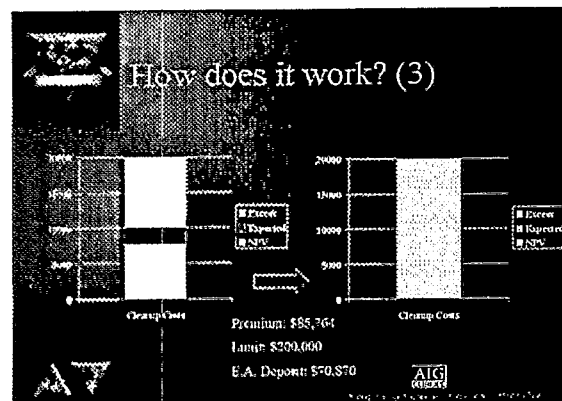
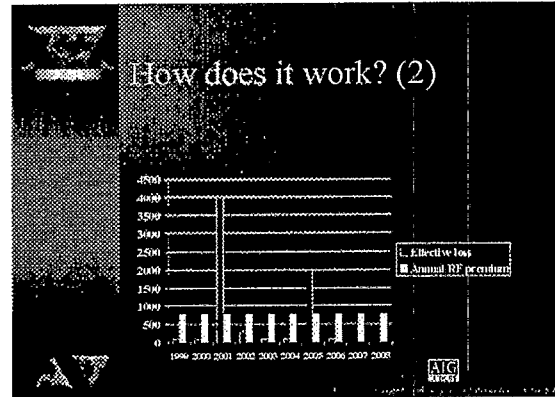
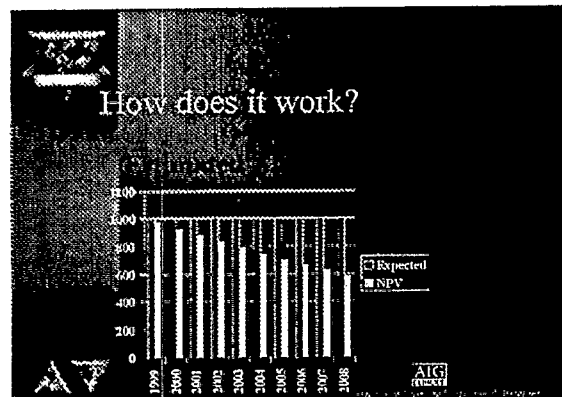


Environmental Protection Programs

- ▼ Manuscript Policy Forms.
- ▼ Expected Costs are discounted.
- ▼ Excess coverage is provided.
- ▼ Rewards for favorable loss experience.

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Case studies

- ▼ Single site acquisition
- ▼ New company

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Single Site Acquisition (1)

Overview:

- ▼ A company for sale owned a contaminated location which deterred prospective purchasers.
- ▼ Brownfield developer was willing to purchase property and clean it up.
- ▼ Seller wanted assurance that developer had the ability and financial support to accomplish.

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Single site acquisition (2)

Problem:

- ▼ By acquiring a contaminated property, the Brownfield Company could be held liable for all environmental conditions, old and new, at the subject site by virtue of holding title to the property.
- ▼ The remedial action plan for the site required financial assurance for closure and post-closure activities.

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Single Site Acquisition (3)

Solution:

- ▼ **Cleanup Cost Cap** to protect against cost overruns associated with the known conditions.
- ▼ **PLL Select** was purchased to protect against liability arising from unknown pre-existing and new pollution conditions at the subject site.


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New Company

Overview:

- ▼ A large company estimated outstanding environmental liabilities in the \$400 million range for a portfolio of properties.
- ▼ The company's objective is to divest the assets and liabilities to form a new company.


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New Company (2)

Problem:

- ▼ The liabilities represented the cost to complete or begin remediation at the sites which were all in various stages of cleanup.
- ▼ Some locations were owned, others were non-owned where the company was a potentially responsible party.


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New Company (3)

Solution:

- ▼ **Cleanup Cost Cap** to protect against cost overruns associated with the known conditions at owned locations as well as liability at non-owned sites as required by environmental statutes.
- ▼ **Cleanup Cost Cap** attached at 110% of the total estimated liabilities and was purchased by the New Company.

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Claims Scenario 1 Cleanup Cost Cap

▼ SIR: 7,100,000 Claims : 2,800,000

▼ **Cause of Loss**

- Additional contaminated sediment discovered at site
- Additional costs due to construction of access roads for equipment access to implement remedial activities.
- Contaminated sediment could not be excavated as originally proposed resulting in increased sediment being excavated.

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Claims Scenario 2 Cleanup Cost Cap

▼ SIR: \$2,260,000 Claims : \$1,200,000

▼ **Cause of Loss**

- Additional contaminated soil discovered at site.
- Original cost estimate included costs associated with UST upgrades, project planning, pre-construction activities and capital improvements, was considered to be a part of the Remedial Action Plan.
- Laboratory analysis, consulting costs, ... not included in the cost estimate from the consultant

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Claims Scenario 3 Cleanup Cost Cap

▼ SIR: 2,670,000 Claims: 7,800,000

▼ **Cause of Loss**


- Groundwater remediation costs were greater
- Additional costs were due to difficulties in site geology.
- Unknown pollutants
- Asbestos discovered

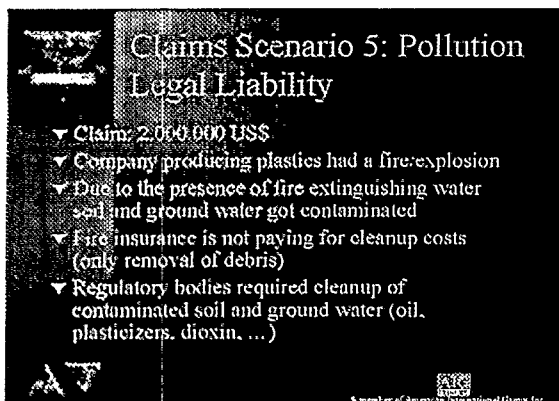
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Claims scenario 4: Pollution Legal Liability

- ▼ Claim: 10,000,000 US\$
- ▼ Polluted site was investigated in detail
- ▼ Regulatory agency issued no further action letter
- ▼ Unfortunately NFA letter had provision clause (can be revised)
- ▼ Contaminants, local situation, adjacent properties and re-evaluation show need for clean-up

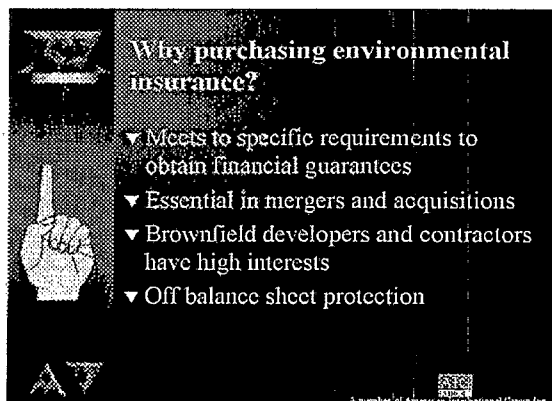
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Claims Scenario 5: Pollution Legal Liability

- ▼ Claim: 2.000.000 US\$
- ▼ Company producing plastics had a fire/explosion
- ▼ Due to the presence of fire extinguishing water soil and ground water got contaminated
- ▼ Fire insurance is not paying for cleanup costs (only removal of debris)
- ▼ Regulatory bodies required cleanup of contaminated soil and ground water (oil, plasticizers, dioxin, ...)

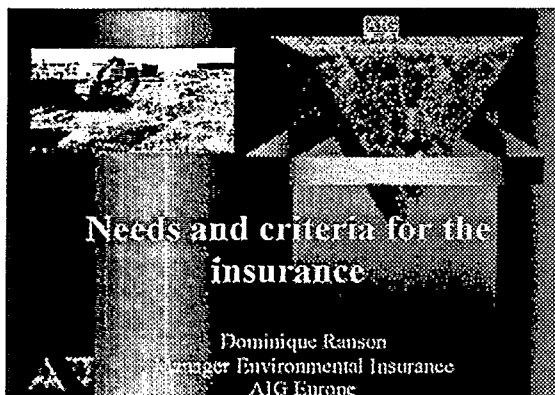
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Why purchasing environmental insurance?

- ▼ Meets to specific requirements to obtain financial guarantees
- ▼ Essential in mergers and acquisitions
- ▼ Brownfield developers and contractors have high interests
- ▼ Off balance sheet protection

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Needs and criteria for the insurance

Dominique Ranson
Manager Environmental Insurance
AIG Europe

SITE-SPECIFIC VERIFICATION OF SOIL VAPOR EXTRACTION

Michael Altenbockum¹ and Oliver Kraft²

1. ABSTRACT

In 1998 data from a number of soil-vapor remediation projects have been reviewed in a research project. The results revealed that most of the reviewed projects showed deficits in important features as field testing procedures, technical standards and criteria for starting, implementing and stopping soil-vapor remedial action. The results also made clear that there is a big demand for standardized procedures and technical guidance in dealing with volatile contaminants in the unsaturated zone.

The German Association of Remediation Engineers (ITVA) will publish directions in the near future that will provide standards for field-testing and data collection. Together with a recently published direction by the environmental state authorities of Nordrhein-Westfalen / Germany, these two publications will provide technical standards as well as criteria to evaluate the effectiveness of soil vapor remediation projects. They also deal with quality control and quality assurance (ITVA) and strategies for terminating soil-vapor remedial action (LUA).

If remedial goals cannot be met, a key number for the evaluation of remedial effectiveness is defined as the specific energy consumption. If specific energy consumption is calculated as being not within tolerable limits, it is suggested that the remedial concept has to be reviewed critically or remedial action should be terminated.

2. INTRODUCTION

In 1998 environmental authorities in Nordrhein-Westfalen launched a research- and development-project to investigate different approaches to soil vapor extraction (SVE) in practical remedial projects. The aim of the research project was as follows:

1. Explore the state-of-the-art of this technology which is meant to be a proven technology,
2. compile the fundamental knowledge about SVE,
3. develop guidelines for SVE remedial practice which should end up in a guidance document and
4. define the frame conditions for an optimized application of this technology.

In the research project, data from one hundred remedial projects and 146 treatment plants from all over Germany were collected and evaluated. To avoid any bias it was made sure that not more than four projects per source were used. The sources were consulting companies, cities, counties, state agencies and others, public and private. Furthermore, laboratory testing has been carried out to gain a broader knowledge about the extraction properties of contaminants under ideal, laboratory conditions.

When evaluating the collected field data, the main focus was put on the following points:

- Field tests of extractions before starting remedial measures,
- documentation of remedial goals and rationale for their specification,
- documentation of procedures to evaluate the effectiveness of remedial action (e.g. effective radius of extraction, extractability of contaminants, mass balance, etc.).

¹ Altenbockum & Partner, Geologen – Aachen, Germany. <http://www.altenbockum.de>

² Altenbockum & Partner, Geologen – Aachen, Germany. <http://www.altenbockum.de>

The following points are given to summarize the results of the data evaluation:

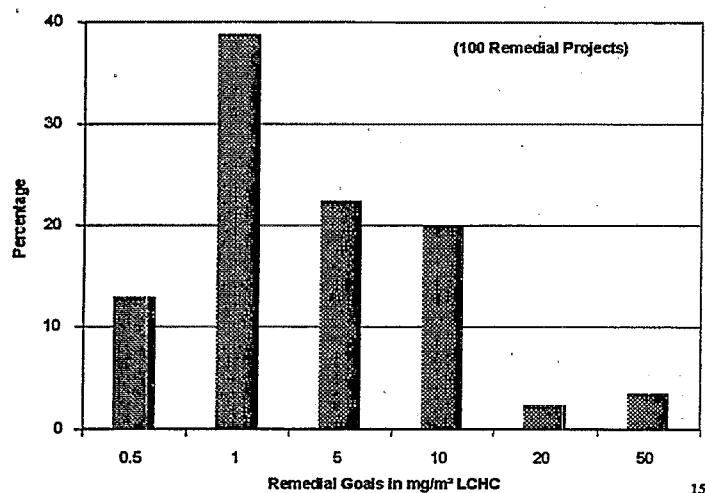
Field-testing before remedial measures:

- In only sixty-five percent of the evaluated case studies extraction tests were carried out in the field before remedial measures were started.
- The duration of the tests ranged from a couple of hours to 99 months [which, in the second case, led to the conclusion that no further remedial action is necessary in this case!].
- In 26 percent of the field tests there were no provisions to treat the off gas.
- None of the field test data sets were considered and implemented in the subsequent design of the treatment plan. Frequently, it was concluded that the process applied during the test would also be the best process for the remedial measures.

Remedial goals:

In Germany, remedial goals are usually specified as numeric goals - as numbers. The specification of these numbers can be named more or less arbitrary because it is frequently done without consideration of the site conditions. Mostly, remedial goals were set up by supervising authorities. Having a look at the numbers that were used as remedial goals, it looks like a "Who has the strictest regulations"-contest has evolved between authorities in charge (Figure 1). The result was that in more than 70 % of the cases, the remedial goals could not be met.

Figure 1: Comparison of remedial goals in field applications (LUA 2001).



Another number that is usually specified by supervising authorities is the off-gas concentration. A technical standard by the German Association of Engineers (VDI) from 1999 provided guidance by giving numbers as maximum levels for contaminant off-gas concentration. These numbers have become mandatory for many, if not the most remedial measures. However, these maximum emission concentrations have to be criticized especially in housing areas, where the maximum concentration levels are obviously too high.

But using adequate technical features and the appropriate technical design of the plant could reduce this problem. In most cases, the off-gas is treated by adsorption of contaminants on activated carbon. It is well known that moisture content plays an important role in the performance of the activated carbon. Adsorption on activated carbon is much less effective with moist gas. There is no activated carbon producer in Europe who gives any warrant for the performance of his activated carbon with moist gases.

With feed gases having the moisture content of natural soil vapor and contaminant concentrations around or below 50 mg/m^3 , the performance of the activated carbon is not really good and the contaminated soil vapor could not be treated properly. Nonetheless, clean-up criteria and remedial goals are specified in this range every day.

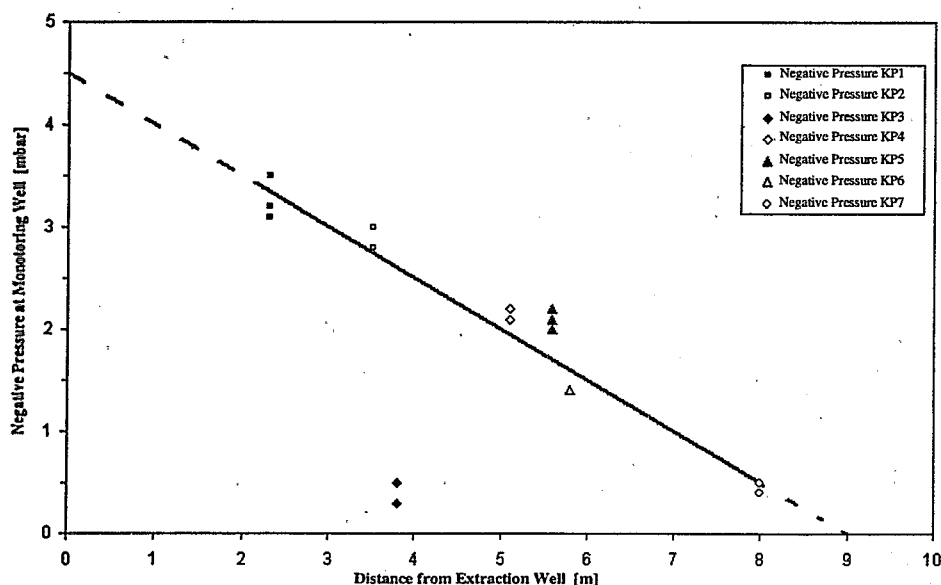
Performance and effectiveness of remedial action:

Not all substrates are suitable for using soil vapor extraction as the remedial measure of choice. So, the minimum result of a soil vapor extraction test is to evaluate if soil vapor extraction is an adequate remediation technique or it is not suitable for the given site conditions. The one criterion that is directly connected to substrate properties is the determination of the soil volume influenced by the extraction. The proof for the influenced volume is the determination by measurements of the under-pressure in neighbored monitoring wells. This determination of the range is used to prove that a negative pressure could be established in the full extension of the contaminated zone.

Data for this determination are gathered during the extraction test and the actual remediation in a representative monitoring grid. Frequently, qualitative tests like smoke candles are used, but data revealed from these kinds of tests are not representative and therefore the conclusions about effectiveness based on those kinds of data are not objective. On the other hand, it is an open question if data gathered from quantitative measurements are only numbers describing negative pressure conditions or if those numbers can be used to evaluate the effectiveness of a remedial measure. To come closer to an answer for this question, we should have a close look at the theory and at some results from laboratory and field tests.

In 1997, the German Association of Engineers published mathematical approaches for the determination of the treatment ranges of SVE. These approaches used ideal conditions (homogeneous sediment with no organic content and zero moisture). Based on these theoretical approaches and depending on some boundary conditions (e.g. screen length, screened zone of the subsurface, diameter of the well, grade of ground surface sealing), it provides an equation and also an analytical solution which allows to calculate the under pressure of a point at a given distance from the well and therefore to calculate the width of the treatment range of SVE. It is well known that in most of the 'real world' cases the conditions in the subsoil are everything but ideal, and they usually cannot be explored in very deep detail. It is therefore more than questionable if mathematical models are really helpful.

Information could again be gained from the research project described several times before, although during the information collection only a limited number of representative data sets could be found. For comparable soil types, in this case fine to medium sand, something like a general trend could be found. This trend was checked in a remediation test at a dry-cleaners site by extracting vapor from different extraction wells in different constellations and monitoring seven wells by under-pressure measurements. Here, negative pressure has been controlled several times during the one-week test. Figure 2 shows a diagram of the results, which were surprising, since obviously there is a negative linear dependency between the under-pressure in the monitoring wells and the distance between monitoring wells and the extraction well. This statement is true for all monitoring wells except KP3, which shows significantly less under-pressure. An explanation for this phenomenon could be found in the files: a massive concrete foundation could be detected between the extraction well and this particular monitoring well, lowering the radius of influence in this direction. All in all, it has to be considered that it is not really clear if other specific site conditions had an influence of the data from this particular field test, since we were not able to further investigate the specific conditions with regards to other inhomogeneities.

Figure 2: Determination of treatment zone diameters (FlächenRecycling, 2000).

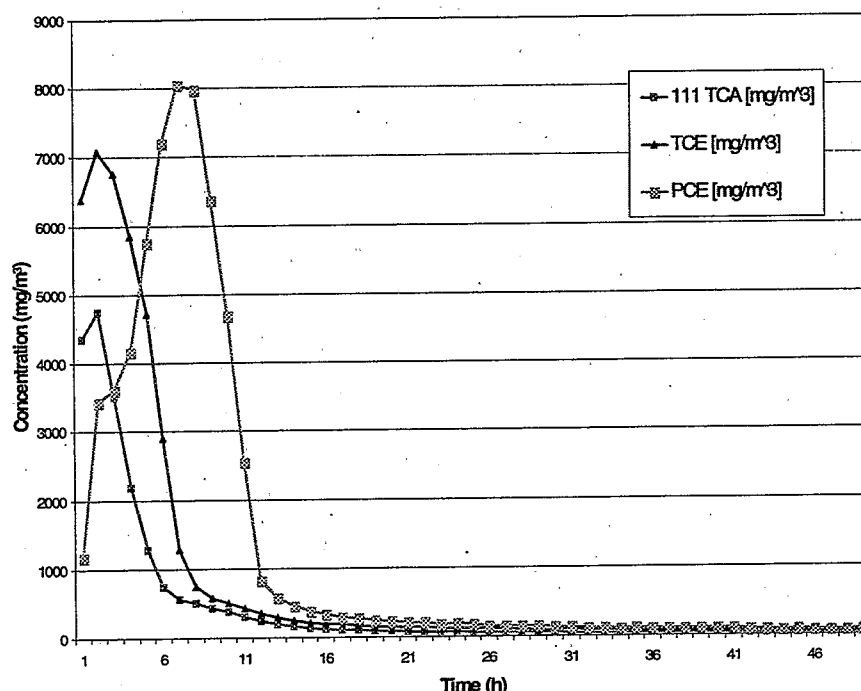
But the effectiveness is not only dependent from site / subsurface conditions, but also from specific properties of the contaminant. To evaluate the extractability of different chlorinated hydrocarbons standardized laboratory tests were also part of the research project. Those tests have been carried out by using a column filled with 1.8 kg of fine sand and 20 g of chlorinated hydrocarbons. Moisture content has been set to 90 % and the temperature during the test was adjusted to 20° C.

Different test series have been done with negative pressures of 1, 5, 10 and 25 mbar, these pressures can be reached in field tests and remedial action under good field conditions. Figure 3 shows a typical example of a concentration curve that was revealed with negative pressures of 10 mbar. Other tests with different negative pressures showed similar results. The concentrations curves of 1,1,1-trichloroethane (111-TCA), trichloroethylene (TCE) and tetrachloroethylene (PCE) are different due to the natural gas law and the Henry constant.

In the beginning, the concentration is high. The reason is the balanced condition in the closed laboratory system. After a while, concentrations decreased rapidly and after a test duration of 48 hours, the efficiency of the extraction was detected to be low and not sufficient. No single test showed a contaminant removal higher than ten percent within the test period. If concentrations had remained stable, treatment times of several years would have been necessary to achieve a sufficient contaminant removal.

These results from evaluation show that in remedial practice, there are a lot of unknowns that have to be taken into account in the planning of soil vapor remedial action. Some of those questions about the status of soil vapor extraction in practice can be summarized as follows:

- What are optimal conditions for SVE in the subsoil?
- What is the influence of moisture, temperature and organic carbon content?
- How can optimal conditions be established?
- What happens with the contaminants in the subsoil under these optimal conditions?

Figure 3: Contaminant concentrations in the Extraction Tests at 10 mbar Negative Pressure (LUA 2001).

3. DEVELOPMENT OF SUFFICIENT REMEDIAL CONCEPTS

In 1997 the Federal German Soil Protection Act was released. This besides a lot of other things it states, that if sufficient suspicion of a hazard is given, further investigation may be required. But when the act was released, some people may have been disappointed, because no evaluation criteria, no numbers for the evaluation of soil vapor concentrations to specify the need for a soil gas remediation were given. Soil vapor is not mentioned at all in this act.

Yet, there are no guidance's available to classify contaminant concentration levels in the soil gas. However, the soil protection act requires the use of numeric quality standards and orientation values (for soil) during decision making as a basic principle. But still, some people need these numbers also for soil vapor extraction.

All decisions according to the Federal German Soil Protection Act should be based on the evaluation of risks from the contamination on different receptors. According to the law, these receptors are water, soil and human health. One exemplary question is, why should the same concentrations of a contaminant pose an identical level of hazard to different receptors?

In Germany only the state of Hessen has identified orientation values for the evaluation of soil gas contamination (Table 1). But these numbers were not designed as limits to decide whether to start remedial action or not. They have been set up to function just as indicators if further investigations should be carried out, the decision about remedial action has to be based on these further investigations, which should focus on the evaluation of the different pathways mentioned above. These investigations include analysis of contamination in solids, groundwater and indoor ambient air as well as the conduction of column tests (leachate prognosis).

Table 1: Orientation values for soil gas concentrations (LUA 2001).

Orientation Values for Soil Gas			
	<i>Groundwater</i>	<i>Indoor ambient air</i>	<i>Soil</i>
Σ LCHC	5 mg/m ³	5 mg/m ³	5 mg/m ³
canc. LCHC	1 mg/m ³	1 mg/m ³	1 mg/m ³
Σ BTEX	5 mg/m ³	5 mg/m ³	5 mg/m ³
Benzene	< 1 mg/m ³	< 1 mg/m ³	1 mg/m ³

With defining orientation values under the described conditions, the state of Hessen showed that they have realized the problem of strict regulations just based on numbers without taking into account the circumstances of any unique case. We should keep in mind that especially for soil vapor contaminant concentrations unique criteria are obviously the wrong approach. The pathways have to be investigated. These are the ambient air and the leachate.

If the evaluation of the pathways results in the decision, that there is no hazard, no action will be necessary. If some indicators for hazards are found, the need for remedial measures must be stated. One of those indicators may be adequate concentrations of volatile contaminants in the soil vapor.

The evaluation of results from soil vapor investigations can be very difficult, because frequently soil gas data lack reproducibility. Practical experiences have shown that these data sets are very often not reproducible by repeated sampling and measurements in the field. Some of the potential reasons are:

- Further influx of contaminants,
- missing documentation of the sampling procedures,
- matrix effects in the non-saturated zone of the subsoil, and
- unknown additional soil vapor properties (e.g. moisture-content).

It is obvious that authorities responsible for the Federal Soil Protection Act and the underlying ordinance knew, that it is not possible to derive soil vapor contaminant concentrations plausibly from solids-concentrations and vice versa. Therefore, soil gas concentration values are missing in these regulations. As true as this statement is, it doesn't help in the daily remedial practice.

The definition of a hazard is one step towards a remedial action. The other one is a remedial investigation, which must document the need for remedial measures. With respect to this, the main point of a remedial investigation should not be the continuing examination of site conditions but more the development of remedial strategies to avoid or reduce hazards in the particular case.

The remedial investigation has to prepare and support the official decision making process on the type and extent of the remedial measures. It should include interim remedial goals and also an evaluation of the applicability and sustainability of potential technological options. The general goal is always to reduce contaminant potential.

4. DIRECTIONS AND REGULATIONS

To support the steps mentioned above, a number of general rules and regulations have been developed by the German states and in engineering associations. These directions and regulations have been designed to formulate the requirements of the different investigation steps according to the Federal Soil Protection Act as well as to standardize methods and techniques used during the investigational work.

As an approach to standardize appropriate procedures and techniques used with SVE remediation projects, the German association of remediation engineers „ITVA“ will issue direction for SVE field tests in fall 2001. The research and development project mentioned above was taken as one basis for those general rules. The direction includes clear recommendations for the duration, the technologies, the sampling, documentation and data-evaluation. Some important points will be described briefly in the following part of this paper.

It should be obvious that a SVE field test should be the basis of any SVE remedial action, but the results of the R & D project in Nordrhein-Westfalen showed clearly that the accomplishment of a reproducible field test is not a standard at all. Table 2 summarizes the technical features of a standardized SVE field test. With this standard it will hopefully be possible that field tests reveal datasets that allow the evaluation of the extractability with respect to the subsoil conditions and that can be used as a basis for an appropriate SVE plant design. It will also make it possible to compare results from different sites.

Table 2: Standards for SVE field-testing (ITVA 2001).

- **Duration of Field Test:** 5 - 10 days;
- **Technical setup:**
 - Design of extraction- and monitoring wells:
 - Inner diameter: 50mm, 1 m tubing, 2 m screen-tubing
 - Gravel-package: 0.5 m clay, 2.5 m gravel
 - Distance between extraction- and monitoring well: 5m and 10m
 - Water- (= particle-) separator;
 - Compressor: 250±50m³/h, 240±30mbar; 2.4±0.4kW
 - Adsorption-unit: 1x200 liters, 70 - 80 kg activated carbon
- **Sampling:**
 - Feed gas after 0.1h, 3.0h, 24h, 48h, 96h (=the end of the test)
 - Off gas after 24h, 48h, 96h (=the end of the test);
- **Documentation of the sampling;**
- **Sampling with field measurement of volumetric flow rate, temperature, moisture in feed and off gas streams;**
- **Evaluation of results regarding the need for remediation, estimation of consumption of activated carbon and energy, development of a sampling and analytical program for the remedial action, short report.**

The technology to perform the extraction testing is suggested according to internationally accepted standards. Remarkable is the waiving of an additional safety filter unit behind the adsorber. The safety filter can be ceased in routine five-day tests. However, it may be necessary if contaminant mass fluxes are expected to be very high and there is a risk of contaminant breakthrough. This evaluation has to be conducted prior to the test.

For the evaluation of SVE field-test results, a number of datasets are needed. These data can be divided into two groups:

1. Quality assurance data:
 - feed gas temperature,
 - moisture content of the feed gas,
 - oxygen content of the feed gas.
2. Performance data:
 - moisture and dew point of the feed gas,
 - volumetric flow rate,
 - under-pressure in the extraction well,
 - under-pressure in the monitoring wells,
 - contaminant concentration-curve,
 - contaminant mass-flux,
 - energy consumption,
 - specific energy consumption.

To ensure the comparability of contaminant concentration data, only two sampling methods can be accepted as adequate: adsorption of target compounds on activated carbon and gas-samples in crimp-cap VOA-vials in a septum-cap under overpressure. The latter need to be injected directly into the GC in the following analysis procedure. The direction includes helpful information about the selection of the appropriate sampling method.

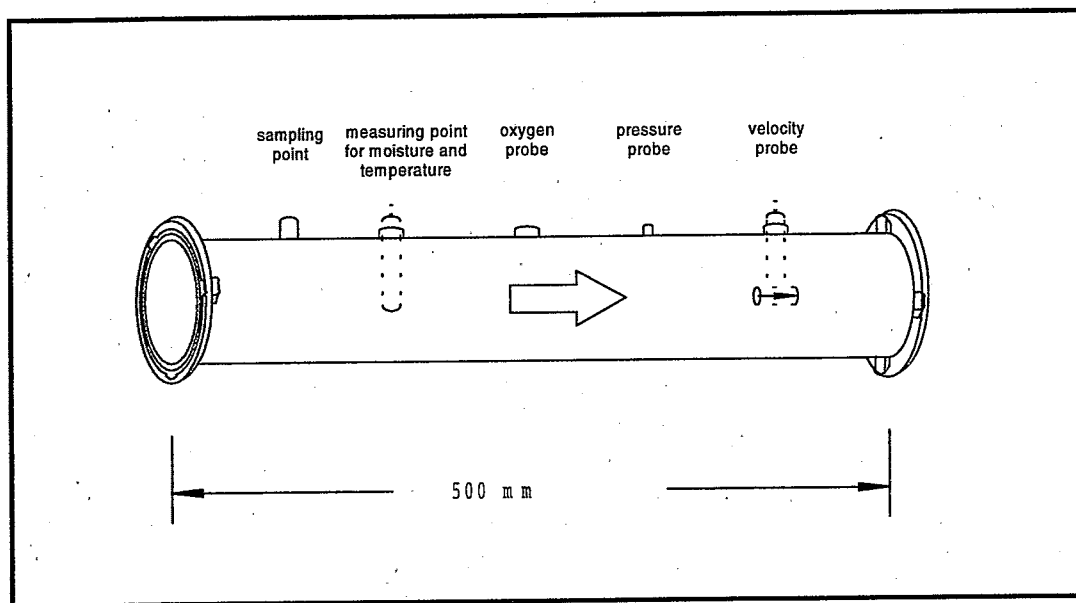
5. QUALITY CONTROL AND QUALITY ASSURANCE DURING REMEDIAL ACTION

The mentioned guidance's and regulations intend to contribute to an improved quality assurance in SVE application. These include the evaluation of applicability of SVE, the planning and design of remedial action and the control and supervision of remedial measures. Most documents are considered being well on-track, because the technical parts are based upon practical field experiences as well as on theoretical fundamentals. Both elements, practical and theoretical, have to be considered

To enlarge the pool of useful and reproducible information as a basis for future SVE projects, there is an obvious need for Quality Assurance (QA) and Quality Control (QC) during all periods of SVE remediation projects. The following issues appear to be of special importance to this subject:

- Sampling as a foundation for quality management (data gathering),
- calculation of mass streams and mass balances, and
- evaluation of data.

Quality assurance and quality control with respect to data gathering can be assured by using appropriate equipment and well-trained staff. All sampling should be done with consciousness about potential sources of error. One comparably simple way to avoid a large number of problems related to the subject of data gathering is to use a mobile sampling tube (Figure 4) with probes for temperature, moisture, flow rate, oxygen-content and negative pressure, which allow a parallel registration of relevant QA/QC-data. Data can be recorded in an electronic data logger; simple connection plugs allow a mobile use at different sampling locations in a plant.

Figure 4: Mobile sampling tube (ITVA 2001).

All relevant data have to be identified in the planning phase and an appropriate monitoring program has to be installed. These data are necessary to calculate mass streams at relevant points within a plant (input - process steps - output) and to set up a mass balance for the complete plant. This is a suitable way to plausibly document mass fluxes and fate of contaminants and water in the plant as well as energy and activated carbon consumption rates.

Figure 5: Characteristic concentration curves and conclusions (LUA 2001).

Parameter	Tendency		Comments
Contaminant Concentration mg/m ³	Tendency increasing		Defendable prognosis of the further concentration curve is not possible Extraction well is not located in the center of contaminated area.
	Tendency unclear		Prognosis of the further concentration is uncertain It needs to be checked if an extension of activity is necessary.
	Tendency decreasing		Extraction well is located in the center of contaminated area Continuous decrease allows for a reliable prognosis.

In combination with the calculation of mass fluxes, the development of contaminant concentrations with time are of great importance with respect to the evaluation of performance during SVE field tests as well as during the subsequent remedial action. Figure 5 shows 3 characteristic concentration curves and gives also general interpretations of the curves.

The examples show that reliable data are the basis for plausible conclusions. Plausible conclusions are essential for the acceptance during negotiations with permitting authorities. Quality assurance / quality control promotes acceptance and allows efficient remediation.

6. STRATEGIES FOR TERMINATION OF REMEDIAL ACTION

The "ideal" SVE remediation project, like any other remediation project, is terminated when contaminant concentrations are below the remediation goal. Then, remedial action is stopped and a monitoring starts to assure the success of the remediation. But what happens if the remedial goals cannot be met in a reasonable time? Then, a new strategy has to be applied. The keyword is feasibility of remedial goals.

There have been some approaches to describe the "effectiveness" of remedial action and to define criteria when to terminate it. The LUA-direction (2001) defines specific energy consumption as the critical criteria. Based on those criteria, it suggests a flowchart for the decision whether or not terminating SVE remedial action (Figure 6).

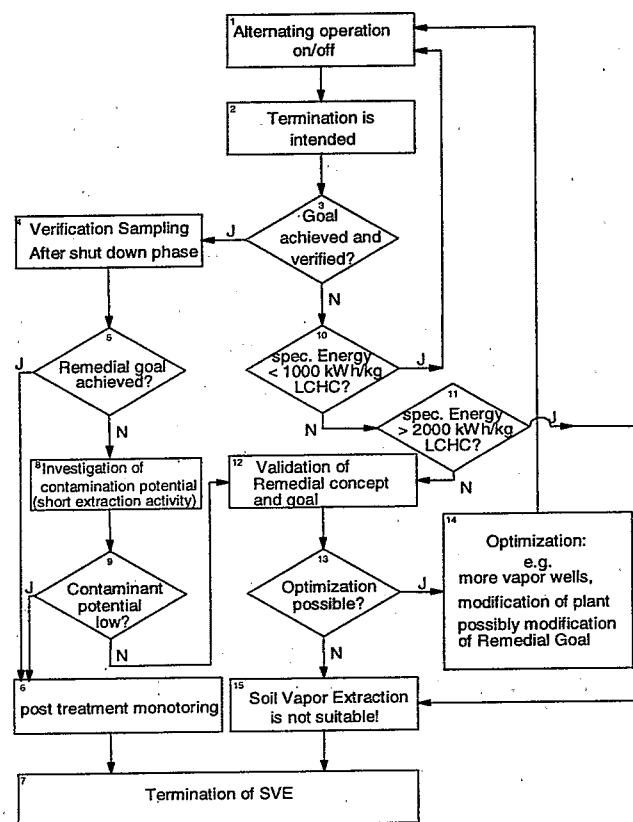
It is defined as the amount of energy that is needed in the particular case to remove one kilogram of chlorinated hydrocarbons (LCHC) from the unsaturated subsoil using SVE. The critical value is 1000 kWh (Kilowatt hours) per Kilogram (kg) LCHC. If less than 1000 kWh/kg LCHC are needed, the SVE is regarded being efficient.

With specific energy consumptions between 1000 and 2000 kWh per kg LCHC, SVE projects should be critically reviewed and a discussion about modifications should be made. Possible solutions to increase the effectiveness of SVE remedial measures may be modifications in plant configuration and/or to continue the remediation in an alternating mode. This means switching the extraction system on and off in specific time intervals.

If more than 2000 kWh of energy are needed to remove one kilogram of LCHC, the soil vapor extraction is insufficient or not a suitable method. Then, SVE remedial action should be terminated and different remedial concepts have to be developed.

The critical values of 1000 or 2000 kWh/kg LCHC have been diverted from the R+D project mentioned a couple of times before. There, more than 400 single extraction phases have been evaluated. The values for specific energy consumption in these project phases have been calculated between more than 8 kg of removed LCHC per kWh and 125.000 kWh for one kg of removed LCHC. Of course, these values depend on the contaminant potential in the subsoil. If there is a significant contaminant potential, there is a good chance of removing the contaminants effectively. On the other hand, the results show clearly that some contaminants cannot be removed no matter what amount of energy is used in the remedial measure.

Data collected in the research project mentioned before showed that a large number of soil-vapor remedial projects have to be evaluated as being ineffective with respect to those criteria (Figure 7).

Figure 6: Decision Support for Termination of SVE remedial measures (LUA 2001).

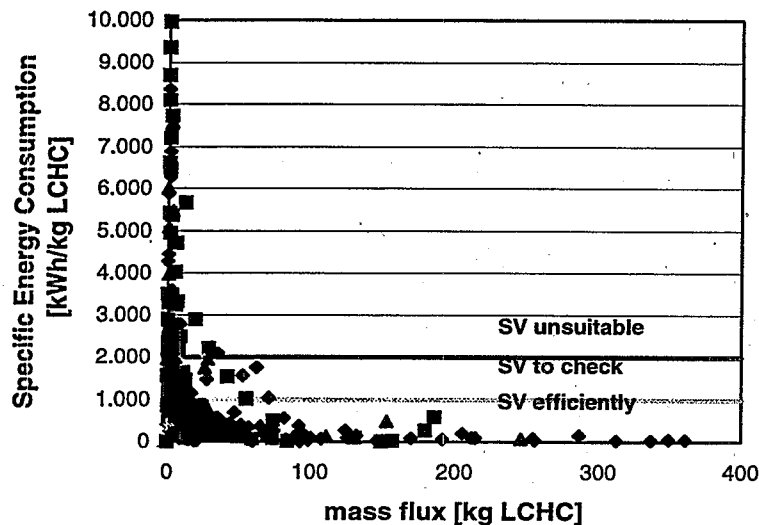
When reviewing the effectiveness of SVE as a remedial measure, the first step should be to check the conceptual approach for plausibility for this particular case. Therefore, the following data are needed:

- Review of all site-specific data (e.g. geology, soil characteristics, contamination in plane and depth, investigations, contaminants/components, development of contaminant levels with time, etc.),
- Components and configuration of the treatment plant,
- Performance data.

If it is found out that the SVE remediation does not work effectively, optimization of the configuration and/or components of the present measure have to be reviewed critically. Possible options for optimization may be more extraction wells or exchange of plant components / modification of technology. Another approach may be in a critical review of remediation goals with respect to site conditions and potential risks from the contamination.

If no concept to optimize the performance of SVE remedial action and remedial goals are found to be suitable, we have to conclude that SVE is not the right technology for the remediation of the subsoil in this particular case and different technologies and approaches have to be discussed.

Figure 7: Specific energy consumption in SVE remediation projects (modified after Altenbockum & Odensaß (1998).



7. CONCLUSIONS

If we want to apply soil vapor extraction and if we want to assure quality, we have to meet the right boundary conditions. In a risk-based approach for evaluation of the necessity of remedial measures, the decision has to be based upon the realistic chance to remove the contaminant-potential for the different receptors. Therefore, the reduction-potential is the crucial factor for the identification of a remedial necessity and for the choice of an appropriate remedial method and technology. Therefore, this decision should not be based on contaminant concentration levels alone.

SVE is without doubt a suitable remediation technology to reduce or remove contaminant-potential in the unsaturated zone if the site conditions and the contaminant potential are appropriate. The suitability of SVE as the remedial method of choice must be proven by a standardized extraction field test. The results of the field test have to be considered in the evaluation of remediation necessity and design of the remedial measure. Field test data must also comprise the deduction of the expected efficiency of the SVE application. The criterion of specific energy consumption is considered to be suitable for the choice of technology as well as for a critical review of an operating remedial measure.

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SITE-SPECIFIC VERIFICATION OF SUFACTANT-COSOLVENT FLUSHING

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1. SUMMARY

The use of surfactant and co-solvent solutions to remove non-aqueous phase liquids (NAPLs) from soils has seen significant research and development activity over the last decade. These soil flushing technologies are now entering the full-scale implementation stage of their development. Since performance assessment is critical to the acceptance of a new technology, methods for assessing the NAPL removal efficiency of soil flushing technologies have been concomitantly evaluated and developed. In this paper, several performance assessment approaches will be described and the use of these approaches during a surfactant-based soil flushing field demonstration project will be detailed.

2. INTRODUCTION – FLUSHING TECHNOLOGY BACKGROUND

Soon after recognizing the importance of removing NAPL sources to reducing long term risks and costs, a number of “flushing” technologies were investigated. In this approach, one or more chemicals (alone or as an aqueous solution) are introduced into the NAPL-contaminated subsurface zone and caused to flow to a collection system under a hydraulic gradient. These chemicals act to enhance either the solubilization or the mobilization of the NAPL, or both. When the additives are co-solvents, the desired result is the solubilization in a homogeneous single-phase solution. Often, such a result is achieved at relatively high co-solvent concentrations, generally greater than 50 wt%. Alcohols ranging from ethanol to pentanol and higher have been evaluated for this application (Jawitz *et al.* 2000, Sillan *et al.* 1998). In some cases, the co-solvents will partition into the NAPL to an extent which alters the interfacial tension properties, thus causing NAPL migration.

The addition of surfactants to the flushing solution can result in both solubilization and mobilization (Butler & Hayes 1998, Chevalier *et al.* 1997, Shiau 1996). Surfactants (surface active agents) are molecules composed of two differing parts: a hydrophobic tail and a hydrophilic head. Because of this, surfactants accumulate at interfaces such as air-water interfaces or water-NAPL interfaces. By tailoring the properties of the surfactant, significant reductions in interfacial tension can be achieved, thus allowing the movement of NAPL trapped by capillary forces. In general, as the concentration of surfactant is increased, the interfacial tension is reduced. However, at a concentration referred to as the “critical micelle concentration” or CMC, surfactants form self-aggregates referred to as “micelles” (Rosen 1989). The CMC is determined by the properties of the surfactant and the aqueous solution. Below the CMC, surfactants are present in solution as individual molecules called “monomers”. Any surfactant added above the CMC will aggregate into micelles, although monomers will still be present at a concentration equal to the CMC. It is the monomer concentration that most effects interfacial tension. Thus, interfacial tension reaches a minimum when the surfactant concentration is 1 CMC and stays fairly constant for surfactant concentrations above 1 CMC.

Micelle structures are such that the hydrophobic tails of the surfactant molecules intermingle to form a hydrophobic core while the hydrophilic head groups form a (usually) spherical outer “shell”. As depicted in Figure 1, molecules of the NAPL compounds will partition into the hydrophobic core, thus raising the apparent solubility of the NAPL compounds in the aqueous solution. The number of surfactant monomer units in a micelle (the aggregation number) is fairly constant for a particular surfactant/solution system. As surfactant is added above the CMC, more micelles, all of approximately the same size, are formed. As a result, the solubilization capacity of the micellar solution increases as the surfactant concentration increases. The increase in apparent solubility can be several orders of magnitude. For example,

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tetrachloroethylene (PCE) solubility increases from 240 mg/L to ~100,000 mg/L upon the addition of 4.0 wt% Alfoterra 145-4-PO sulfate™ surfactant and 16.0 wt% isopropyl alcohol (IPA). Addition of 0.18 wt% CaCl_2 to the system raises PCE solubility to 700,000 mg/L (Duke Engineering 2000).

Flushing solutions are delivered and extracted via screened wells. Thus, proper design, installation, and operation of the well field and flow rates are critical to the success of *in situ* flushing technologies. Subsurface flooding simulators, such as UTCHEM (Brown *et al.* 1994, Delshad *et al.* 1996), combined with hydrogeological and biogeochemical data for the subsurface formation, NAPL, and flushing solution allow for design optimization and the estimation of process efficacy.

3. PERFORMANCE ASSESSMENT FUNDAMENTALS

The performance of soil remediation technologies has traditionally been assessed using groundwater monitoring and/or soil sampling. The former assumes that a unique relationship exists between the aqueous concentrations observed at a monitoring well and the mass or volume of NAPL in adjacent portions of the aquifer. Unfortunately, this assumption is patently invalid because of the diffusion and solubility limitations of the NAPL components; therefore groundwater monitoring is inaccurate for assessing the performance of a NAPL remedial action. Under ideal conditions, the analysis of soil samples will yield a satisfactory performance assessment. However, this requires that the samples be representative of the unsampled regions and that all sediments and interstitial fluids are recovered from soil samples. Thus, spatial variations in NAPL distribution and soil heterogeneities must be minor for soil sampling to be an accurate performance assessment method, and proper sampling tools and sampling procedures must be followed to maximize recovery of all solids and liquids from a soil sample. Otherwise, the number and size of samples necessary to obtain an accurate estimate of the NAPL mass within a subsurface volume must be impractically large. One of the main issues related to soil sampling is the representative elementary volume (REV) which is the volume of soil required to yield a single sample representative of the region being sampled (Mariner *et al.* 1997). In many cases, the REV is larger than the volume of typical soil samples. Thus, accurate information concerning the local NAPL saturation and distribution is difficult to obtain using soil samples.

To address issues related to REV, a relatively new method of NAPL characterization and remediation performance assessment, called partitioning interwell tracer tests (PITTs), has been introduced (Jin *et al.* 1995). In this technique, an aqueous solution containing multiple tracers is injected via wells into the NAPL-contaminated formation. The tracers are selected to provide a range of water-NAPL partition coefficients ranging from conservative (non-partitioning) tracers to highly partitioning compounds. Most of the tracers are straight- and branched-chain alcohols. The tracers are then recovered at another well or set of wells. The appearance of each tracer at the recovery well is a function of the retardation of transport caused by partitioning of the tracers into the NAPL phase. In fact, the tracer concentration vs. time relationship observed at the recovery wells is quite similar to that observed during the chromatographic analysis of compounds – tracers which do not partition into the NAPL appear first and at relatively high concentrations. Those that have high partition coefficients appear later and tend to have significant peak tailing. Examples of tracer recovery during PITTs in the presence and absence (or near absence) of NAPL are shown in Figure 2a and 2b, respectively. The mathematical manipulation of the tracer concentration curves yields an estimate of the NAPL residual saturation (S_n) in the subsurface region swept by the tracers (Wilson *et al.* 2000, Mariner *et al.* 1997, Jin *et al.* 1995, Dwarakanath *et al.* 1999, Rao *et al.* 2000, James *et al.* 2000). Similarly, interfacial tracers can be used to estimate the NAPL-water interfacial area (a_{nw}) (Rao *et al.* 2000). Multi-level sampling (MLS) devices positioned between the injection and extraction wells can yield information about the vertical variation in NAPL saturation (James *et al.* 2000, Sillan *et al.* 1998).

PITTs have a number of limitations and cannot be applied to assess all remediation technologies. Current methods of analyzing PITT data assume that the following conditions exist:

- 1 Tracer partition coefficients (K) are accurately known
- 2 Reversible sorption of tracers to sedimentary organic matter has been quantified
- 3 Tracers penetrate all parts of the NAPL zone including:
 - a. Free-phase NAPL zones
 - b. Low intrinsic permeability or low relative permeability zones
- 4 Multiple tracers with a wide range of Ks used
- 5 Sufficient time provided to assess tracer signals from all parts of NAPL zone.

Due to these assumptions, the ability of PITTs to accurately account for pooled free-phase DNAPL is limited. In addition, high levels of soil heterogeneity can result in tracers having reduced or no access to low permeability zones, for example into clay lenses. Thus, PITTs most effectively estimate NAPL saturation when the NAPL is fairly uniformly distributed as residual ganglia (Wilson *et al.* 2000).

A measure of remediation performance can be obtained by comparing the results of PITTs performed before and after the remediation. The use of PITTs for this purpose is relatively independent of the remediation technology employed. When applied to the performance assessment of in-situ thermal remediation (ISTR) technologies, the timing of the post-treatment PITT as well as the thermal stability of the tracers used will be an issue. Because of their inherent similarities, PITTs and enhanced flooding technologies are particularly well-matched. When conducted prior to the soil flushing process, the PITT design can be incorporated into the remedial flood design, due to the similar flow dynamics. The assumptions listed in the paragraph above must be true for both the pre- and post-remediation PITTs. If the flushing process alters any of these properties, then they must be separately determined for each PITT. For example, if the flushing process alters the makeup of remaining NAPL, then the water-NAPL tracer partition coefficients must be measured again. Such may occur when a surfactant is used to remove a complex NAPL consisting of organics with variable viscosities from the subsurface. A complex NAPL treated using a thermal technology may experience similar difficulties in the use of PITTs due to the preferential removal of NAPL components of low volatility. Flushing processes may also affect the sorption of tracers to the soil, for example if the fraction of organic content of the soil is altered. Therefore, tracer soil sorption must be characterized before and after the remediation.

Finally, monitoring of the extracted flushing solution as well as samples obtained from MLSs and other sampling wells during the flushing process will yield a direct and real-time measurement of remediation performance. The mass of NAPL compounds solubilized by the flushing solution is calculated by integrating the contaminant mass flow rate (concentration times flow rate) vs. time data for the extracted fluid. The sum of this solubilized mass and the mass, if any, of free product NAPL recovered yields the amount of NAPL removed due to the remediation. This amount can then be compared to initial NAPL mass estimates or to NAPL removal estimates obtained from soil sampling or PITT data. A mass balance on injected chemicals should also be conducted by integrating concentration data obtained from extraction wells to evaluate the efficiency of hydraulic containment. This is important as high residual concentrations of injected chemicals following surfactant/co-solvent treatment may cause unintended migration of solubilized chemicals beyond the treatment zone. Monitoring for injected chemicals and contaminant beyond the treatment zone, particularly in locations down gradient to and beneath the treatment zone, can also provide data about whether hydraulic control of fluids has been maintained during the soil flushing process. Finally, maintaining a log of the water levels at all wells to create potentiometric surface maps can provide further supporting evidence that proper control over injected fluids was maintained during flooding operations.

4. EXAMPLE –SURFACTANT FLUSHING FIELD DEMONSTRATION AT U.S. MARINE CORPS BASE CAMP LEJEUNE

4.1 Camp Lejeune Background and Site Details

In 1999, a surfactant enhanced aquifer remediation (SEAR) demonstration, funded by the Environmental Security Technology Certification Program (ESTCP), was conducted to remove a chlorinated hydrocarbon DNAPL present in the subsurface beneath the central dry-cleaning facility (Building 25, Site 88) at U.S. Marine Corps Base Camp Lejeune, North Carolina. The main contaminant was tetrachloroethylene or PCE, a common dry-cleaning solvent. At this site, groundwater contamination of the shallow and intermediate aquifers has resulted from the storage and disposal of PCE and Varsol™ dry-cleaning solvents. The latter is a mineral spirit-type solvent. The footprint of the demonstration well field was 20 ft x 30 ft (6.1 m x 9.1 m), and the DNAPL contaminated zone targeted for remediation was the bottom 5 ft (1.5 m) of the shallow aquifer. The total aquifer pore volume treated was approximately 6600 gallons (25.0 m³). By design, the ESTCP SEAR Camp Lejeune demonstration treated only a portion of the entire DNAPL source area. In addition to the subsurface treatment by SEAR, the ESTCP SEAR demonstration was the first to incorporate above-ground treatment of the SEAR extraction well effluent (i.e., groundwater, surfactant, and DNAPL) by pervaporation and micellar-enhanced ultrafiltration (MEUF) for the objective of surfactant recycle. The objectives of this demonstration were to: 1) validate *in situ* surfactant flooding for DNAPL removal; 2) promote the effective use of surfactants for widespread DNAPL removal; 3) demonstrate that surfactants can be recovered and reused; and 4) show that surfactant recycle can significantly reduce the overall cost of applying surfactants for subsurface remediation.

The locations of the three surfactant injection, two hydraulic control, and six extraction wells relative to Building 25 are shown in Figure 3. Six MLS wells each with three vertical sampling locations in the 16.5 to 20 ft bgs range were positioned within the well field (not shown). Injection and extraction wells were screened across the bottom portion of the shallow aquifer from approximately 15 to 20 ft (4.6 to 6.1 m) below ground surface (bgs), which coincided with the depth interval of the DNAPL contaminated zone. Varsol™, present as an LNAPL in the upper portion of the shallow aquifer (8 to 10 ft bgs) was not targeted for remediation. However, some Varsol™ was present as a component of the PCE DNAPL, varying between approximately 2-14 wt% across the test zone, and was removed incidentally with the PCE DNAPL.

The DNAPL zone at Building 25 was primarily in the shallow surficial aquifer at a depth of approximately 16-20 ft (5-6 m), and includes an area that extends about 20 ft (6 m) north of the building. The DNAPL occurs immediately above and within a relatively low-permeability layer of silty sediments (hereafter referred to as the basal silt layer). The basal silt layer occurs from approximately 18 to 20 ft (5.5-6 m) below ground surface (bgs) and grades finer with depth from a sandy silt to a clayey silt until reaching a thick clay layer at about 20 ft (6 m) bgs. Characterization activities associated with the SEAR demonstration revealed that this fining downward sequence can be roughly divided into three permeability zones: the upper zone (~16-17.5 ft bgs; 4.9-5.3 m bgs), the middle zone (~17.5-19 ft bgs; 5.3-5.8 m bgs), and the lower zone (~19-20 ft bgs; 5.8-6.1 m bgs). The site conceptual model, or geosystem, is shown in cross section in Figure 4.

The upper zone is generally characteristic of the overall shallow aquifer, which is primarily composed of fine to very-fine sand and is the most permeable of the three zones. The hydraulic conductivity (K) of the upper zone is estimated to be about 5×10^{-4} cm/sec (1.4 ft/day). The hydraulic conductivity of the middle zone, which is composed predominantly of silt, is estimated to be approximately 1×10^{-4} cm/sec (0.28 ft/day), or about five times less permeable than the upper zone. The lower zone is composed predominantly of clayey silt, with a hydraulic conductivity that is believed to be approximately 5×10^{-5} cm/sec (0.14 ft/day) or perhaps even lower, although the permeability of the lower zone is not well characterized at this time.

4.2 Camp Lejeune Performance Assessment

Soil core samples were obtained prior to SEAR activities to locate DNAPL, to delineate the boundaries of the DNAPL contamination and to characterize the subsurface hydrogeology. The soil core samples were preserved in the field with methanol to minimize contaminant losses by volatilization from the soil samples. Subsequent to the soil coring, a free-phase DNAPL recovery process was implemented. A pre-SEAR PITT was then conducted during May/June 1998 to measure the volume and relative distribution of DNAPL present in the test zone before surfactant flooding. The results of this pre-SEAR PITT indicated that approximately 74-88 gal (280-333 L) of DNAPL were present in the test zone (Duke Engineering 1999), which was later determined to be an underestimate. Average DNAPL saturations were found to be highest in the portion of the test zone adjacent to Building 25, at about 4.5% saturation (expressed as an average DNAPL saturation over the swept pore volume between an interwell pair of injection and extraction wells).

The SEAR demonstration at Building 25 included multiple phases of field activities that spanned 143 days. The surfactant flood was initiated with an 8-day water flood, followed by a 58-day surfactant injection period between April 6 and June 3, 1999, a 34 day post-SEAR water flood, 40 day post-SEAR PITT, and 3 days of post-SEAR soil sampling. Post-SEAR sampling was conducted under continued water flooding conditions to avoid re-entry of DNAPL from untreated contaminated zones adjacent to the treated zone. The injected SEAR solution contained 4.0 wt% Alfoterra 145-4-PO sulfateTM surfactant, 16.0 wt% IPA, and ~0.17 wt% CaCl₂ and was injected at 0.4 gpm (1.5 L/min). Calcium was used as the sole electrolyte to avoid ion-exchange induced mobilization of soils fines in the subsurface. The total extraction rate was 1.0 gpm (3.8 L/min). Groundwater samples were collected from all extraction wells (EX1-EX6) and from three of the six MLSs throughout the demonstration to monitor the recovery of both PCE and injected chemicals from the treatment zone. Not all of the selected MLS sampling points produced sufficient sample volumes for analysis due to the fine-grained nature of the soil. A gradient in DNAPL contamination with distance from the building was inferred by examining the PCE concentration curves for the six extraction wells. At EX-03 and EX-6, the extraction wells farthest from the building, PCE concentrations remained low, not exceeding 20 mg/L throughout the entire SEAR demonstration, most likely indicating that there was little DNAPL in the vicinity of these locations.

A significant increase in the extraction well effluent PCE concentration was observed in several extraction wells due to surfactant flooding. At extraction well EX1, the effluent PCE concentration increased from an average of approximately 200 mg/L to about 2,800 mg/L at the peak breakthrough. At EX4R, the PCE concentration increased from 80 mg/L to approximately 1,000 mg/L at the peak. In addition to the extraction wells, PCE concentrations were also measured in MLS points located next to EX1 and EX4R. At MLS-4T (16.5 ft bgs), the PCE concentration at the start of the surfactant flood was 5 mg/L. The effluent PCE concentration was seen to increase rapidly to 10,860 mg/L before declining to non-detectable concentrations at the end of the post-SEAR PITT. This is an excellent indication that the surfactant was highly effective in solubilizing and remediating DNAPL in the upper zone in the vicinity of MLS-4T. Relatively high aqueous PCE concentrations were observed at MLS-1B (18.5 ft bgs) at the end of the demonstration suggesting that some DNAPL still remained in the zone adjacent to MLS-1B. The MLS surfactant and IPA concentration data indicate that little surfactant injectate penetrated (i.e., swept) the lower-permeability basal silt layer compared to the upper zone. Thus, little or no DNAPL was removed at these lower depths. This result can be attributed primarily to the preferential flow of surfactant injectate through the more permeable upper zones and consequential bypassing of the lower zones, and secondarily to some surfactant sorption and/or biodegradation.

In addition to enhancing the solubility of the DNAPL, the surfactant flood also enhanced the recovery of free-phase DNAPL as a result of lowering the interfacial tension of the DNAPL. Because of the presence of a thick aquitard at the site and because of its greater mass removal efficiency, mobilization of DNAPL during the surfactant flood was desirable and intended by design. A total of 76 gal (288 L) of PCE was recovered during the surfactant flood and subsequent water flood, of which approximately 32 gal (121 L) of PCE were recovered as solubilized DNAPL and 44 gal (167 L) as mobilized free-phase DNAPL.

A table showing the volume of solubilized and free-phase DNAPL recovered per well is provided as Table 1.

Table 1: Recovery of Solubilized and Mobilized PCE from Camp Lejeune Wells.

Extraction Well	Solubilized PCE Recovered (gal)	Mobilized PCE Recovered (gal)
EX1	19.4	15.3
EX2	1.9	8.7
EX3	0.1	0.0
EX4	NS	3.6
EX4R	9.4	5.2
EX5	0.9	2.6
EX6	0.1	0.0
RW1	NS	2.0
RW2	NS	2.0
Other sources	0.0	4.6
Total	31.8 gal (120 liters)	44.0 gal (166 liters)

NS: not sampled, PCE concentration data was only collected at the extraction wells

The post-SEAR PITT was conducted, along with soil core sampling, to measure the volume of DNAPL remaining in the test zone after the surfactant flood. During the post-SEAR PITT, the unexpected sorption of an impurity in the surfactant formulation caused interference with the partitioning tracers, making the post-SEAR PITT data unusable. The sorption of the surfactant impurity caused false detection of DNAPL as a result of tracer partitioning into the sorbed surfactant impurity. The surfactant manufacturer, Condea Vista, has tentatively identified the sorbing substance as a byproduct of the manufacturing process and has developed an alternative synthesis route that avoids the production of this impurity. However, soil column studies at The University of Texas at Austin indicated that extended water flooding following injection of the "purified" surfactant is still required to avoid tracer retention when calcium is used as the sole electrolyte. This indicates the possible formation of a calcium surfactant complex that retards the partitioning tracers. The change in the background tracer sorption behavior caused by the SEAR process violated assumption #2 listed in Section 2 for analysis of PITT data.

Due to the difficulties encountered with the accurate interpretation of the post-PITT data, SEAR performance was ultimately evaluated by examining combinations of the mass recovery of DNAPL at the extraction wells, and the pre- and post-SEAR soil sampling data. The pre-SEAR soil samples were not used to generate an initial DNAPL volume estimate because the sampling frequency used was intended to locate DNAPL, delineate the extent of DNAPL contamination and to identify an appropriate location for the SEAR well field. Additionally, during the intervening period prior to the surfactant flood a free-phase DNAPL recovery effort was conducted and there was difficulty in quantifying the amount of free-phase DNAPL removed. Therefore, any DNAPL volume estimate generated from the pre-SEAR soil samples would not accurately represent pre-SEAR conditions.

The post-SEAR soil sampling data consisted of 60 soil samples collected at 12 locations over the contaminated portion of the aquifer, and was used to generate a three-dimensional distribution of the DNAPL volume remaining in the test zone following the surfactant flood. Continuous cores were collected from the bottom 3 feet of the aquifer (representing the DNAPL contaminated zone) and then subdivided into six inch core samples. The lateral distribution of DNAPL indicates that the majority of the DNAPL that remains in the test zone is located near the building, between wells EX1 and EX4. DNAPL volume decreases away from the building, in the area between wells EX2 and EX5, and very little DNAPL is present in the portion of the test zone that is farthest from the building, between wells EX3 and EX6. The vertical distribution of remaining DNAPL indicates that DNAPL was effectively removed from the more permeable sediments, generally above about 17.5 ft (5.3 m) bgs, and that DNAPL

still remains in the lower permeability basal silt layer. These results are not unexpected, given that the highest pre-SEAR DNAPL saturations were near the building, as well as the expectation that it would be most difficult to remove DNAPL from the lowest permeability sediments at the site.

A geostatistical analysis of the post-SEAR soil sampling results was used to interpolate the post-SEAR soil sampling data to generate a DNAPL volume estimate, as well as to assign error bars to the resulting estimates. Analysis of the post-SEAR soil core data indicated that approximately 5.2 ± 1.6 gal of DNAPL remain in the zone that was effectively swept by the tracers and surfactant (i.e. the zone above approximately 17.8 ft bgs). In addition, data analysis from the post-SEAR soil cores indicated that approximately 23.5 ± 5.5 gal remain in the mid-to-bottom zone that was not effectively penetrated by the tracers or surfactant (i.e. from 17.8 ft bgs down to the clay aquitard). The initial PITT estimated that the volume of DNAPL in the test zone before the surfactant flood was approximately 81 ± 7 gals (306 ± 26 L). It was concluded that the total volume of DNAPL present in the test zone before the surfactant flood is best represented by both the volume of DNAPL measured by the pre-SEAR PITT plus the volume of DNAPL estimated (from soil core data analysis) for the zone below 17.8 ft bgs, for a total pre-SEAR DNAPL volume of approximately 105 gal (397 L). Adding the 76 gallon estimate of DNAPL recovered at the extraction wells to the 29 gallon estimate of DNAPL remaining in the test zone by soil cores also yields a similar pre-SEAR DNAPL volume of 105 gallons. Thus the surfactant flood recovered approximately 72% of the DNAPL from the entire demonstration zone, including all zones above the aquitard (Duke Engineering 2000).

With respect to the efficiency of hydraulic control during the surfactant flood, IPA recoveries were sufficiently high, approximately 88%, but surfactant recovery was lower, on the order of 78%. The surfactant data declined much faster compared to the IPA concentrations in the middle and bottom zones during the late-time period of the test, which suggests surfactant sorption and/or biodegradation. Potentiometric surface maps of the shallow aquifer generated for several phases of the demonstration show that hydraulic control of injected fluids was effectively maintained, with the exception of a minor loss of hydraulic control at HC1 during Phase II of the surfactant flood. This loss was caused by a slightly exaggerated gradient between injection well IN1 and HC1 with the higher viscosity surfactant fluids. This temporary loss of hydraulic control was confirmed by increasing IPA concentrations with time at a monitoring well (RW03-not shown), peaking on July 27 (Day 112 of the test) at 2,798 mg/L (compare to IPA injectate concentration = 160,000 mg/L). However, recovery of 88% of the injected IPA by the end of the demonstration suggests that any loss of hydraulic control was very minor. During the post-SEAR water flood and post-SEAR PITT, the potentiometric surface maps show that hydraulic containment was fully established and maintained for the remainder of the demonstration. In support of this, IPA concentrations at well RW03 dropped to 428 mg/L with the last monitoring sample collected on August 27. Hydraulic control monitoring conducted beneath the test zone (i.e., below the aquitard) showed that no downward migration of injected chemicals and contaminant occurred during the SEAR demonstration.

4.3 Camp Lejeune – Performance Assessment Lessons Learned

With respect to performance assessment, while considerable data was collected for evaluating pre- and post-SEAR DNAPL saturations, only a subset of this data was usable. The pre-SEAR PITT provided valuable baseline DNAPL conditions in the test zone, although later data suggests that, because of the permeability contrast in the basal silt layer, the initial PITT did not detect a portion of the DNAPL that was present in the bottom 1-2 ft (0.3-0.6 m) of the shallow aquifer. The pre-SEAR PITT did, however, accurately detect and measure the volume of DNAPL in the accessible (i.e., higher permeability) zone above approximately 18 ft (5.5 m) bgs. Regarding the future use of PITTs, the influence of permeability heterogeneities as well as potential interference by surfactants when calcium is used as the sole electrolyte should be carefully considered in design. Finally, performance assessment is inherently limited when the remedial measure treats only a portion of a NAPL contaminated zone due to the potential for reinfiltration of contamination from untreated zones. Thus, when high quality performance assessment data is essential, as in this ESTCP technology validation effort, it is necessary to design the remedial technology to treat the entire source zone.

5. CONCLUSIONS

Surfactant and co-solvent flushing technologies offer attractive options for NAPL source area treatment. Soil core analysis and PITTs are the two most likely performance assessment tools. Soil sampling may provide significant cost savings for small homogeneous sites. Also, when a high degree of vertical heterogeneity exists, soil sampling may provide confirmation of DNAPL conditions in the lowest permeability zones. However, PITTs will be more cost effective and provide more defensible performance assessment for large-scale sites with a moderate degree of heterogeneity. Great care must be taken in the planning, execution, and analysis of PITTs in order to yield meaningful information. Although PITTs can be extremely powerful tools, they have limitations, some of which were evidenced during the Camp Lejeune field demonstration. In practice, the dual use of PITTs and soil core sampling can yield sufficient performance validation information.

6. ACKNOWLEDGEMENTS

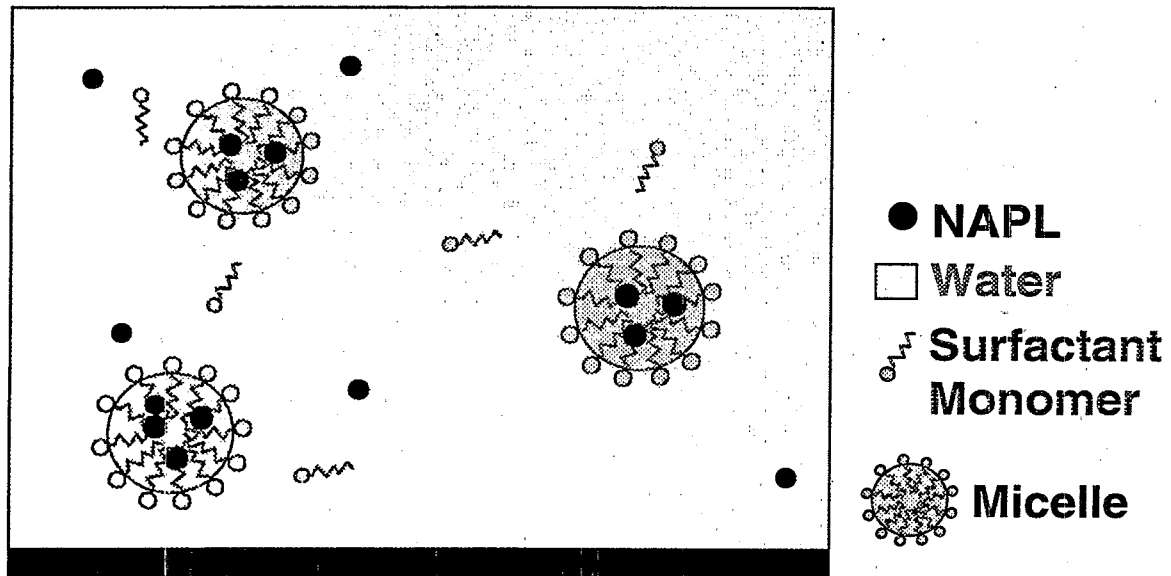
Much of the information regarding the Camp Lejeune field demonstration project was excerpted from the draft Final Technical Report for the project as well as the Final Report (Duke Engineering 2000). Many of the general concepts regarding performance assessment for SEAR processes were originally expressed in a workshop entitled "Surfactant Enhanced Aquifer Remediation (SEAR)" which was presented most recently on October 15, 2000 in San Antonio, TX. Material for the workshop was prepared by Duke Engineering and Services (F. Holzmer, H. Meinardus, V. Dwarakanath, J. Londergan), University of Texas at Austin (G.A. Pope), and U.S. EPA (L. Vane). The workshop was sponsored by the U.S. Navy and facilitated by Battelle.

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Figure 1: Surfactant solution containing surfactant monomer and micelles.



*NAPL = non-aqueous phase liquid

Figure 2: Example PITT tracer response curves (Battelle and Duke Engineering 2001).**How to Interpret PITT Recovery Curves:**

- A suite of chemical tracers is injected into the subsurface.
- Generally, the conservative (nonpartitioning) tracer peak will arrive first.
- The nonconservative (partitioning) tracer peak will arrive later, as the tracer is retarded by interaction with DNAPL.
- The difference in peak arrival time and tailing behavior can be correlated to DNAPL saturation.

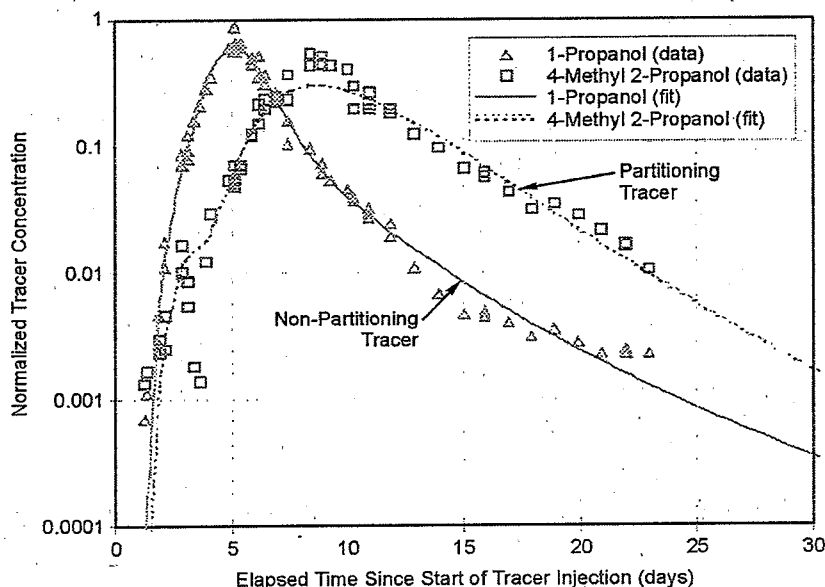
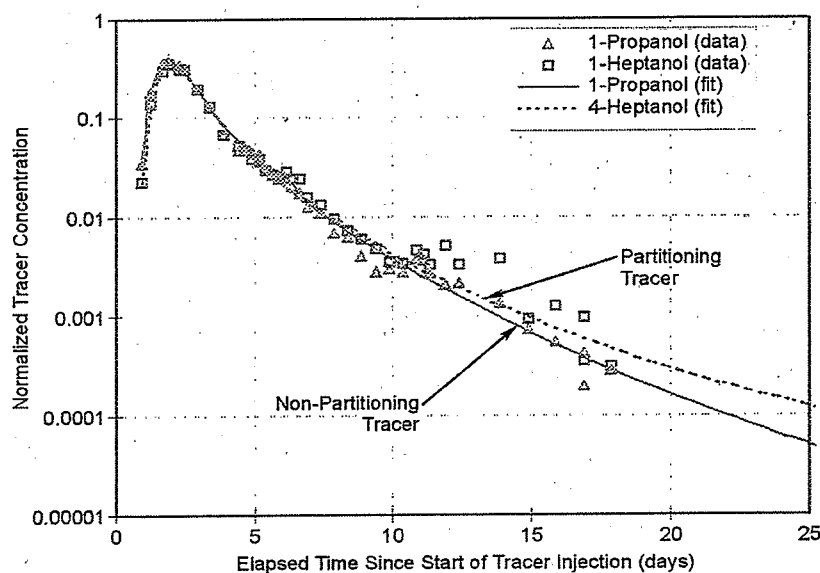
**(a) High Residual NAPL Saturation****(b) Low Residual NAPL Saturation**

Figure 3: Site map of SEAR demonstration at U.S. Marine Corps Base Camp Lejeune. Well field consisted of six extraction wells (EX1-EX6), three surfactant injection wells (IN1-IN3), and two hydraulic control wells (HC1 and HC2). Building 25 is an operational dry cleaning facility.

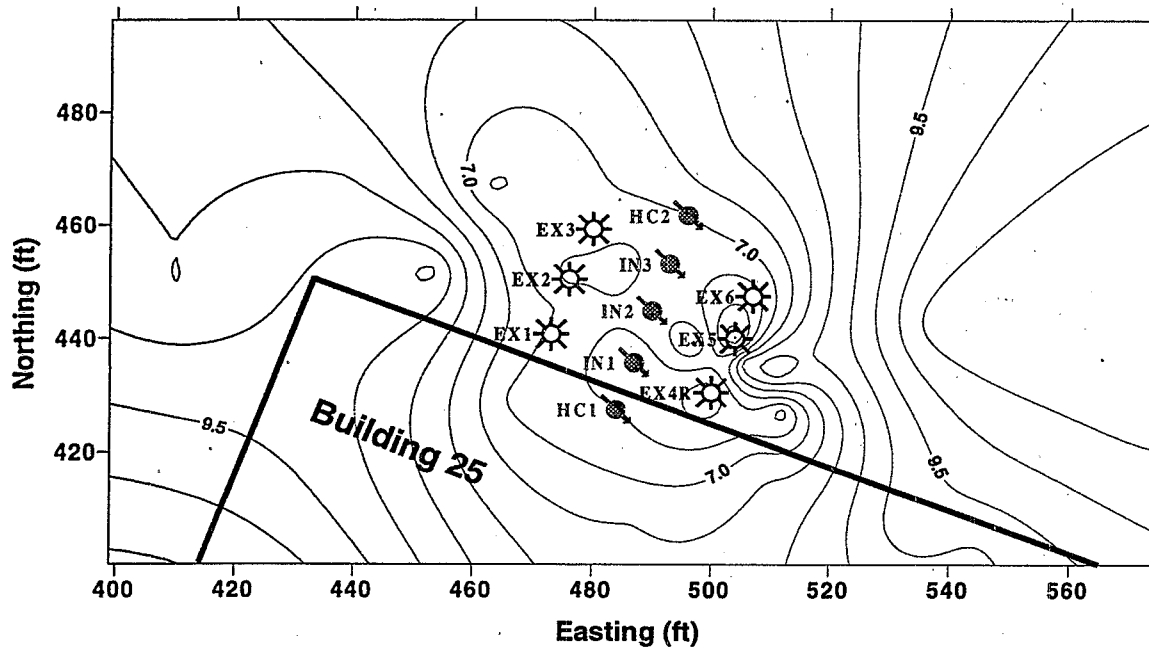
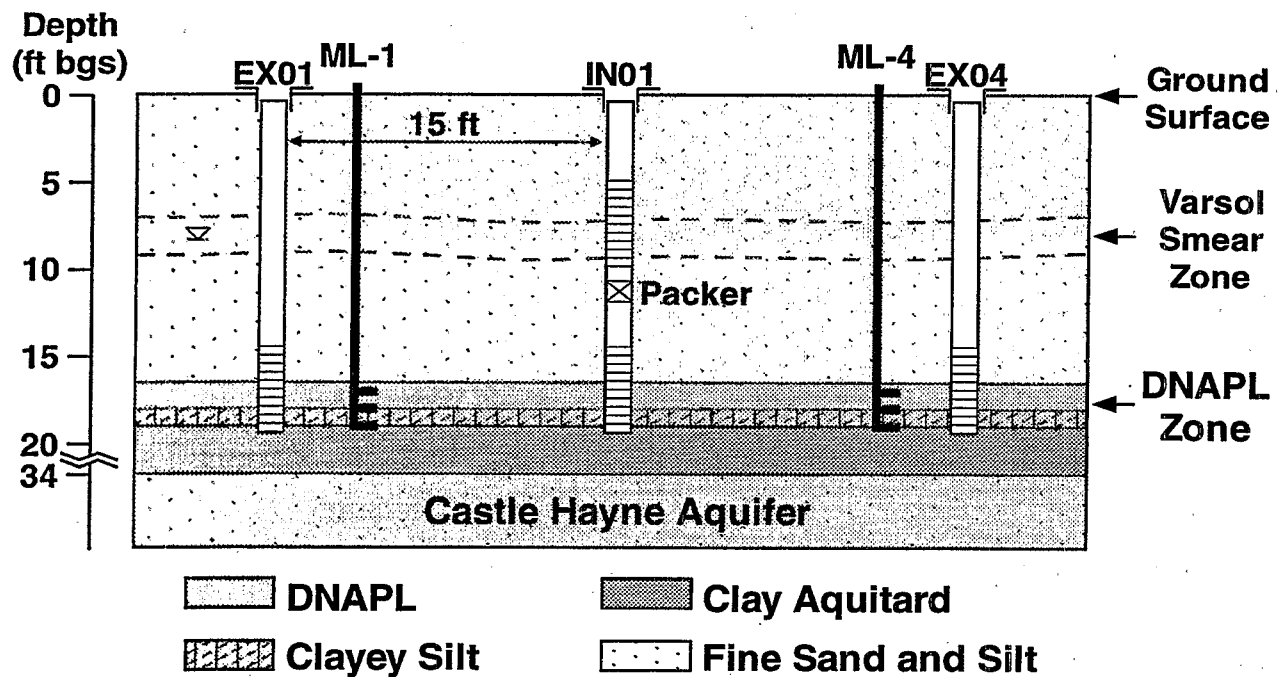


Figure 4: Generalized geosystem cross-section of DNAPL zone at Site 88, Building 25, MCB Camp Lejeune.



8. PRESENTATION VISUALS ~ presented by Leland Vane and S. Laura Yeh

Site-specific Validation of Surfactant/Co-solvent Flushing

Leland M. Vane, Ph.D.
U.S. Environmental Protection Agency
&
S. Laura Yeh
U.S. Navy

2001 NATO/CCMS Pilot Study Meeting
Validation of *in situ* Remediation Performance

Outline

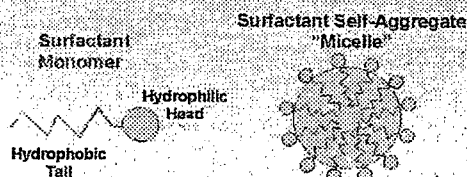
- Overview of Chemical Flooding Technologies
- Performance Assessment (PA) Issues & Methods
- Surfactant flooding PA example: Camp Lejeune demonstration
- Conclusions

Surfactant Flushing/Flooding

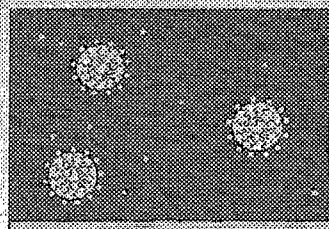
- SEAR stands for:
Surfactant Enhanced Aquifer Remediation
- SEAR involves the injection of surfactants to recover NAPL-contaminants by either enhanced solubilization or mobilization due to interfacial tension reduction.
- May result in a single-phase solution or multi-phase fluid

Surfactants

Surfactants are surface active agents. They are molecules composed of two differing parts: a lyophobic tail and a lyophilic head. This structure leads to the molecule's interesting behavior.



Surfactant Solution – Enhanced solubility of NAPL compounds in micellar solutions – over 100,000 mg/L



*NAPL = non-aqueous phase liquid

Range of Properties of Injected SEAR Fluids

- Anionic Surfactant = 1 to 8 wt%
 - well above critical micelle concentration
- Alcohol = 0 to 16 wt%
 - stabilizes surfactant/contaminant solution
- Ca^{2+} and/or Na^+ = 0 to 1750 mg/L
 - reduces migration of soil fines

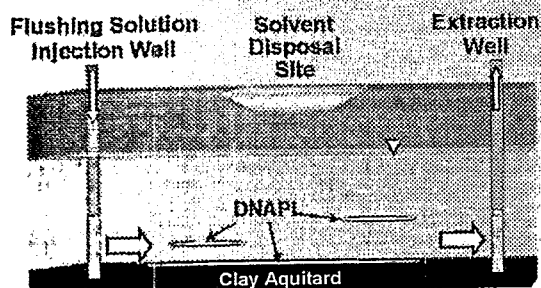
Surfactant Flooding (cont.)

- Surfactant also reduces interfacial tension thereby enhancing NAPL removal through mobilization
- Mobilization requires a competent capillary barrier (aquitard) to prevent vertical DNAPL migration

Co-solvent Flushing

- Co-solvents increase the solubility of NAPL contaminants in a homogeneous one-phase system.
- Generally consist of alcohols above 50 wt% in aqueous solution

Surfactant or Co-solvent Flushing



General Issues for Performance Assessment (PA) of DNAPL Sites

- DNAPLs tend to be found in regions of low permeability
- The typical DNAPL site has:
 - Heterogeneities in permeability
 - Variable DNAPL distribution
- Since DNAPL flows with gravity, data on the depth to aquitard should be collected.

Methods for Evaluating the Volume and Distribution of NAPL for Performance Assessment

- Groundwater monitoring
- Soil sampling
- Partitioning interwell tracer test (PITT)
- Monitor extraction well DNAPL concentrations (amount removed)

PA by Groundwater Samples

- Assumption: A unique relationship exists between the aqueous concentration (at a monitoring well) and the mass or volume of NAPL in adjacent portions of the aquifer

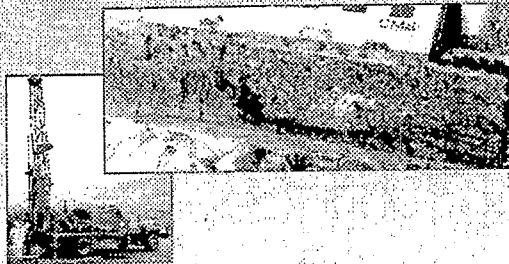
Because of mass transfer limitations, groundwater sampling is an inadequate method for PA of a NAPL remedial action.

PA of Flushing Technologies by Groundwater Samples

- Use to evaluate whether hydraulic control has been maintained
- Use to monitor residual conc. of injected chemicals following treatment.
 - Surfactant, co-solvent if used and contaminant
- **Do NOT** use to assess efficiency of DNAPL removal.

PA by Soil Sampling

Continuous Soil Cores Sampled With Field Preservation



Soil Sampling Methods

Direct push

Geoprobe® with plastic tube liners

Things to avoid

- Wash rigs (lots of water flooding)
- Air rigs (lots of SVE)

Things to do (EPA Method 5035)

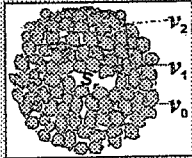
- Use in-field preservation (methanol)

Soil Sampling Methods (cont.)

- Continuous sampling throughout the zone of interest:

- Get samples from critical zones
- \$\$ savings if you do not need upper zone sampled

Soil Sampling Limited by Representative Elementary Volume (REV)



The Accuracy of Soil Samples for Remedial Design

- Range of REV for NAPL in soil = 10^{-10^4} cm^3
- Volume of typical soil sample = $30 \cdot 10^2 \text{ cm}^3$

Issues for PA by Soil Sampling

- Is the sample representative of the area it is selected to represent (REV)?
- Has all of the NAPL present been recovered from each sample?
- Have soil samples been recovered from all parts of the targeted NAPL zone (i.e., from both high and low permeability zones)?

NAPLANAL* Calculates:

- NAPL saturation
- NAPL composition
- VOC concentrations in each phase

*NAPL estimation computer program developed by Duke Engineering and Services

NAPLANAL Data Needs

Field Soil Samples

- Total concentrations for each component
- Volumetric water content
- Soil porosity
- f_{oc}

DATABASE

- K_{oc} for each component
- K_H for each component
- Molecular weight of each component
- Densities
 - Soil, water, air, NAPL

Geostatistical tools (Kriging) Useful for Creating Picture of NAPL at Site

- Interpolation method for determining the average DNAPL volume based on a set of soil samples
- Calculate the error associated with a particular estimate

Partitioning Interwell Tracer Tests (PITTs)

- Conservative and partitioning tracers are injected and monitored at extraction wells/intermediate locations
- Well-suited for flushing-type remediation assessment
- Over 40 PITTs conducted to date
- Developed for DNAPL site characterization by Dr. Gary Pope at UT-Austin and Dr. Dick Jackson at Duke Engineering & Services

PA by PITTs

- PITTs provide measurements on a meaningful scale
 - address REV issue
 - can measure DNAPL in the entire treatment volume swept by tracers
- PITT results and error can be quantified

PITT Assumptions

- Multiple tracers with a wide range of Ks used
- Tracer partition coefficients (K) accurate
- Reversible sorption to sedimentary organic matter quantified
- Tracers penetrate all parts of the NAPL zone:
 - Free-phase NAPL zones
 - Low intrinsic permeability or relative permeability zones
- Sufficient equilibration time provided to assess tracer signals from all parts of NAPL zone

PITT Weaknesses (violations of assumptions)

- Pooled or free-phase DNAPL
 - underestimate of DNAPL saturation if free-phase is not removed
- High soil heterogeneity -
 - results in poor sweep of low permeability zones
 - mobility control may correct for this

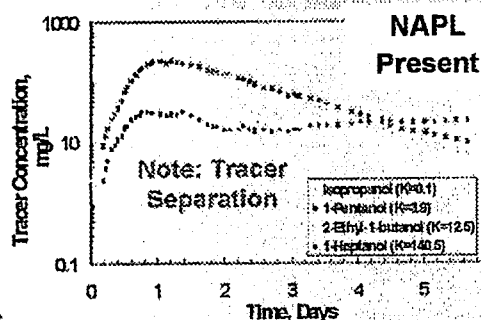


PITT Weaknesses (cont.)

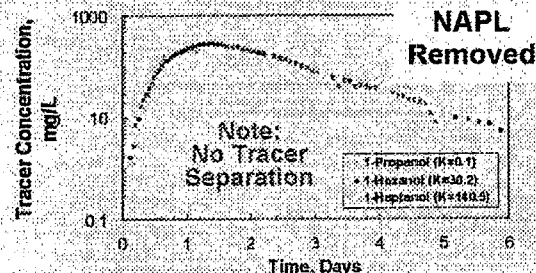
- Affected by spatial variation in NAPL composition and naturally occurring organic matter (measured as f_{oc})
 - K must be measured for different NAPL compositions and f_{oc}
 - inaccuracies in K estimation may result
- For SEAR applications, surfactant complexation with clay fines may be a concern



Pre-SEAR PITT



Post-SEAR PITT



PITTs: Performance Validation

- Difference in DNAPL volume estimates obtained from pre- and post-PITTs indicate level of removal in flushed zone
- Multi-level sampling (MLS) during remediation and PITTs can yield assessment of vertical variations in performance effectiveness



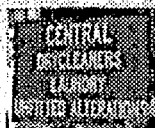
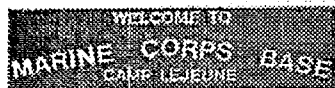
Issues for PA of *in situ* flooding technologies

- Flushing/PITT fluids will tend to flow through high permeability zones
 - Low permeability zones are most susceptible to residual contamination
- Recovery of injected chemicals never 100%
 - Post-treatment monitoring may be required
- SEAR not intended to reduce GW conc. to MCLs
 - DNAPL mass estimates necessary to gauge performance



Example Site

- U.S. Marine Corps Base Camp Lejeune
 - Soil contaminated with dry cleaning solvent (PCE) – Site 88



Surfactant Enhanced Aquifer Remediation with Surfactant Regeneration/Reuse

Lead Organizations:

- Naval Facilities Engineering Service Center (NFESC), Port Hueneme, CA
- U.S. EPA National Risk Management Research Laboratory (NRMRL), Cincinnati, OH and Ada, OK

Collaborators:

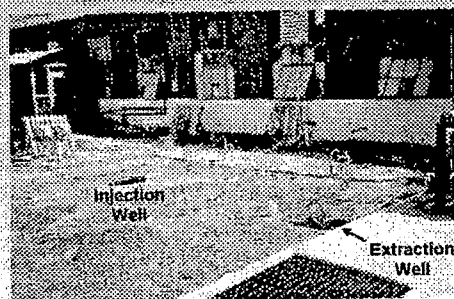
- University of Texas, Austin, TX
- University of Oklahoma, Norman, OK
- Duke Engineering & Services, Austin, TX



Camp Lejeune Demo Zone

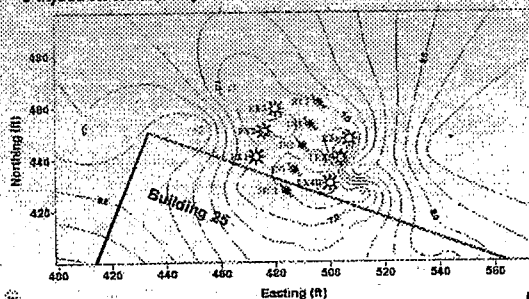
- Size of test zone - 20' x 30' (6.1 m x 9.1 m)
 - Test zone = approx. 25% of DNAPL zone
- Depth to aquitard - 18-20 ft bgs (5.5-6.1 m)
- Soil type - fine to very fine sands and silts
- Hydraulic conductivity = 5×10^{-4} to 5×10^{-5} cm/s
- Primary Contaminant - PCE
 - Initial DNAPL volume ~ 105 gal (~397 L)
- Surfactant injected in bottom 5 ft of aquifer

Camp Lejeune SEAR Well Field

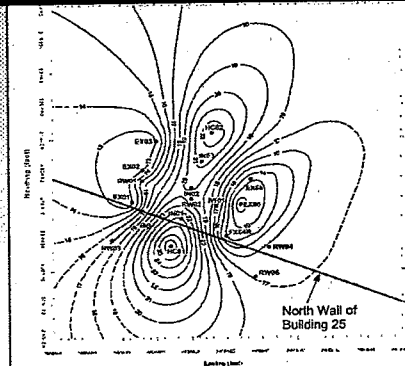


Camp Lejeune Site Map

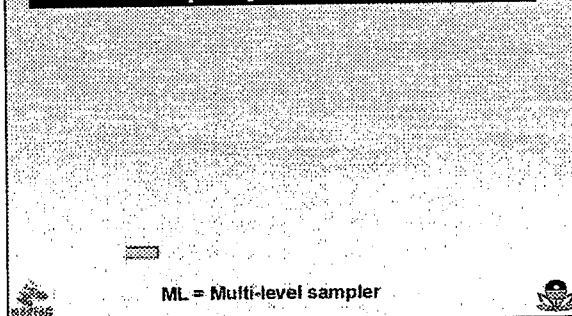
3 injection wells, 2 hydraulic control wells, 6 extraction wells



Potentiometric Surface - Hydraulic Control



Geosystem Cross Section of MCB Camp Lejeune DNAPL Zone



Camp Lejeune Performance Assessment and Monitoring Methods

- Extraction fluid monitoring
- MLS Monitoring during SEAR flood
- Pre/Post Partitioning interwell tracer tests (PITT)
- Pre/Post Soil sampling

Schedule of Camp Lejeune Flooding Activities in 1999

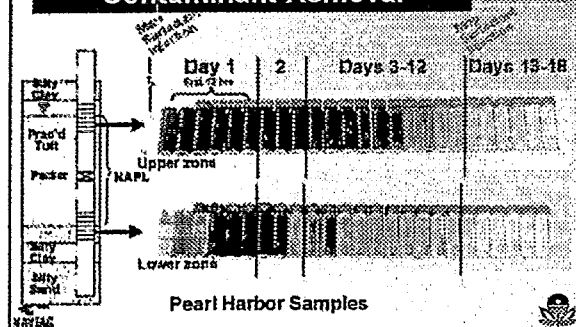
Dates	Activity	Duration
Mar 29-Apr 6	Pre SEAR Water Flood	8 days
Apr 6-May 14	Surfactant Flood I (fresh)	37 days
May 14-Jun 3	Surfactant Flood II (recycled)	21 days
Jun 3-July 7	Post-SEAR Water Flood	34 days
July 7-Aug 16	Post-SEAR PITT (PITT2)	40 days
Aug 16-19	Post-SEAR soil sampling (water flooding continued)	3 days

Total duration of flooding: 143 days

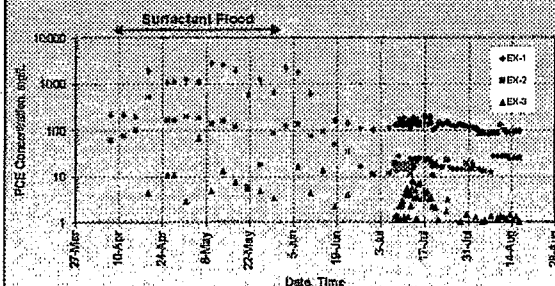
Analysis of Extracted Flushing Solution

- Estimate mass of contaminants recovered
- Estimate mass of surfactant recovered
- Determine if hydraulic control is adequate
- Multi-level samplers monitor delivery of flushing agents to all vertical zones

SEAR Effluent - Evidence of Contaminant Removal



Extraction Well PCE Data



Note: Extraction wells EX-4, EX-5 and EX-6 show similar results.

Estimated DNAPL Recovery Camp Lejeune Extraction Well Data

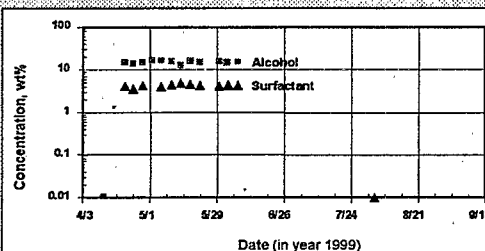
Extraction Well	Solubilized PCE Recovered (gal)	Mobilized PCE Recovered (gal)
EX01	194	153
EX02	1.9	8.7
EX03	0.1	4.0
EX04	NS	3.6
EX04R	0.4	5.2
EX05	0.9	2.8
EX06	0.1	0.0
RW01	NS	2.0
RW02	NS	2.0
Other sources	0.0	4.6
Total	31.8	44.0

NE: not sampled. PCB data only collected at the extraction wells.

Overall PCE Recovered ~76 gal (288 L)

SEAR Flood MLS Data - IPA and Surfactant Conc. at MLS-4T (16.5 ft bgs)

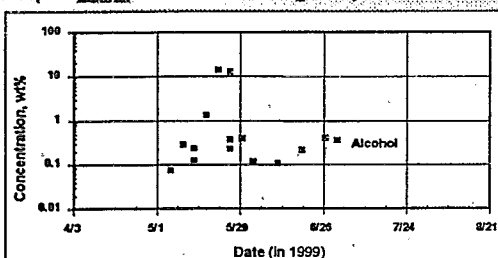
High and Steady Concentrations Indicate Good Sweep of Upper Contaminated Region by SEAR Fluid



56:52 DATE CONTAINED IN:

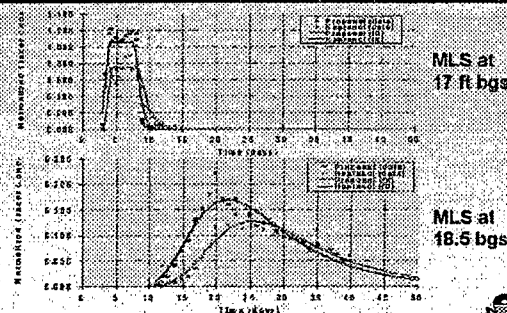
**SEAR Flood Multi-Level Sampler Data –
MLS-4B (18.5 ft bgs) – near aquitard**

Low and Variable IPA Concentrations Indicate Poor Sweep of Lower Contaminated Region by SEAR Fluid



564 DE LOCE-SAGE, LARSEN, AND

Poor Sweep of Lower Perm. Zones



Camp Lejeune PITT1 Results

Ex. Well	Tracer Recovery (%)	Swept Volume (gal)	DNAPL sat'n (%)	DNAPL Volume (gal)
EX01	13	790	3.9	31
EX02	17	1030	0.5	5
EX03	10	540	0.4	2
EX04	14	790	4.5	36
EX05	17	890	1.0	10
EX06	14	740	0.4	3
Total	85	4780	1.8	87

18.1 m³

329 L

Camp Lejeune PITT Results

➤ Initial PITT estimated 81 ± 7 gal (306 ± 26 L) of DNAPL

- PITT did not adequately account for low permeability zones due to short-circuiting through high permeability zones

➤ **PITT2 - Tracer response curves indicated more DNAPL after SEAR**

- False partitioning of tracers to sorbed surfactant
- Nonionic impurity in the surfactant sorbed to aquifer soils

PITT Lessons learned

- Mobility control measures needed to minimize short-circuiting through high permeability zones
- Experiments to test for sorbing impurities in surfactants should be conducted

Estimated Costs (US\$) for Camp Lejeune PITT

- Low Permeability Site, 40 days
 - Pre/post-PITT, 111 yd³: ~\$127,000 each
 - Pre-PITT, 463 yd³: \$182,100
 - Post-PITT, 463 yd³: \$164,500
- High Perm. Site, 23 days
 - Pre-PITT, 617 yd³: \$74,900
 - Post-PITT, 617 yd³: \$71,200

Camp Lejeune Post-SEAR Soil Sampling

12 locations, 60 samples for DNAPL volume estimate

- Continuous cores in bottom 3 ft (1 m) - just above aquitard
- 6 inch core samples
- 1 borehole per 6.6 m²

Soil Sampling PA DNAPL Volume Error Sources

Parameter	Contributor	C _v	% Error
Residual Saturation S _r	organic carbon	58%	23%
	Porosity	9%	
	GC analysis	20%	
Domain Volume V _T	number of borings	6%	16%
	sampling interval	5%	
	Interpolation	14%	
φ	Porosity	9%	9%
DNAPL Volume V _N			29%

Interpretation of Post-SEAR Soil Core Data

- 5.2 +/- 1.6 gal DNAPL remain in zone effectively swept by tracers and surfactant (i.e. above ~17.8 ft bgs)
- 23.5 +/- 5.5 gal DNAPL remain in mid-to-bottom zone that was not effectively penetrated by tracers or surfactant (i.e. from 17.8 ft bgs down to aquitard)

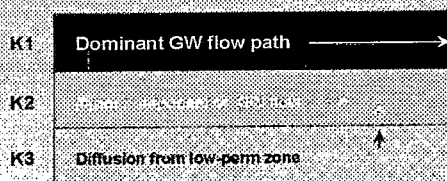
Interpretation of Post-SEAR Soil Core Data

- Surfactant flood recovered between 92% to 96% of DNAPL present in the pore volume that was swept by the pre-SEAR PITT (i.e. above 17.8 ft bgs)
- Little to no DNAPL recovered from zones below 17.8 ft bgs

Interpretation of Post-SEAR Soil Core Data (cont.)

- Surfactant flood recovered ~70% of the DNAPL from the entire zone
 - Mass recovery of DNAPL from extraction wells: ~76 gal (286 L)
 - Initial DNAPL estimate by PITT: 81 ± 7 gallons
 - Final DNAPL estimate by soil sampling: 29 ± 9 gallons (23.5 gal in lower zones)
 - "Amalgamated" initial DNAPL estimate: 105 ± 12 gallons (397 ± 45 L)

SEAR Effectiveness at Camp Lejeune, Site 88



Aqueous dissolution should be significantly reduced since most of the accessible DNAPL (from K1 & K2 zones) has been removed from the dominant ground-water flow paths.

Conclusions on PA Methods for Quantifying NAPL Volume

- Groundwater sampling not valid for even semi-quantitative assessment
- Soil sampling is semi-quantitative:
 - REV limitations
 - potential loss of contaminants
 - uncertainty is not quantifiable
- PITTs are more complex, but when properly designed and implemented, provide a means of accurately and quantitatively measuring NAPL volumes with quantifiable uncertainty.



Conclusions for Flushing Tech. PA

- Multiple PA methods needed for accurate results
 - Soil sampling costly for large treatment volumes.
 - PITTs may not sweep low permeability zones when high perm contrasts exist.
 - Multi-level samplers can identify which zones have been swept by surfactants and the relative removal of DNAPL with depth
- PA must account for heterogeneities and spatial distribution of DNAPL



Acknowledgments

- Duke Engineering and Services
 - Fred Holzmer *et al.*
- University of Texas at Austin
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 - Neeraj Gupta *et al.*



SITE-SPECIFIC VERIFICATION OF IN SITU BIOREMEDIATION

Frank Volkering¹

1. INTRODUCTION

Biological remediation strategies such as in-situ bioremediation, biobarriers and monitored natural attenuation require detailed knowledge of groundwater processes, and especially of biodegradation processes. The information obtained via traditional lines of evidence is not always conclusive or sufficient. Table 1 provides an overview of the traditional characterization methods.

Table 1: Strengths and weaknesses of traditional characterization methods.

Method	Strength	Weakness
Pollutant concentration	specific, quantitative	inconclusive
Degradation intermediates	conclusive, specific, quantitative	not for all pollutants
Mineralization products	conclusive, quantitative	not specific
Geochemical characterization	important process parameters	not specific, qualitative
Microcosm studies	conclusive, specific, semi-quantitative	lengthy, expensive
In situ experiments	conclusive, quantitative	lengthy, expensive

Biochemical techniques, such as DNA/RNA analysis may be used to obtain conclusive and specific evidence for biodegradation, but the evidence is mainly qualitative and as yet only applicable for a limited number of pollutants.

This paper presents a new line of evidence for bioremediation, based on the natural stable isotope composition of organic pollutants. Isotope analysis gives us a view into the pollutant molecules and offers conclusive, pollutant-specific, and possibly even quantitative information on biodegradation processes.

2. THEORY

Isotopes are elements with the same atomic number, but with a different atomic weight. Most elements on earth consist of two or more stable isotopes, as can be seen for the elements occurring in the most common organic pollutants in Table 1 below.

Table 2: Elements of the most common organic pollutants and their isotopes.

Element	Common isotope		Other stable isotopes	
	isotope	%	isotope	%
hydrogen (H)	¹ H	99.985	² H	0.015
carbon (C)	¹² C	98.89	¹³ C	1.11
nitrogen (N)	¹⁴ N	99.63	¹⁵ N	0.37
oxygen (O)	¹⁶ O	99.759	¹⁷ O	0.037
			¹⁸ O	0.204
chlorine (Cl)	³⁵ Cl	75.53	³⁷ Cl	24.47

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For analytical reasons, stable isotope concentrations are expressed using the δ -notation, relating the isotope ratio of a sample to that of a standard reference material. For ^{13}C , the standard material is Vienna PeeDee Belemnite (VPDB), a marine carbonate. The δ for ^{13}C is defined as:

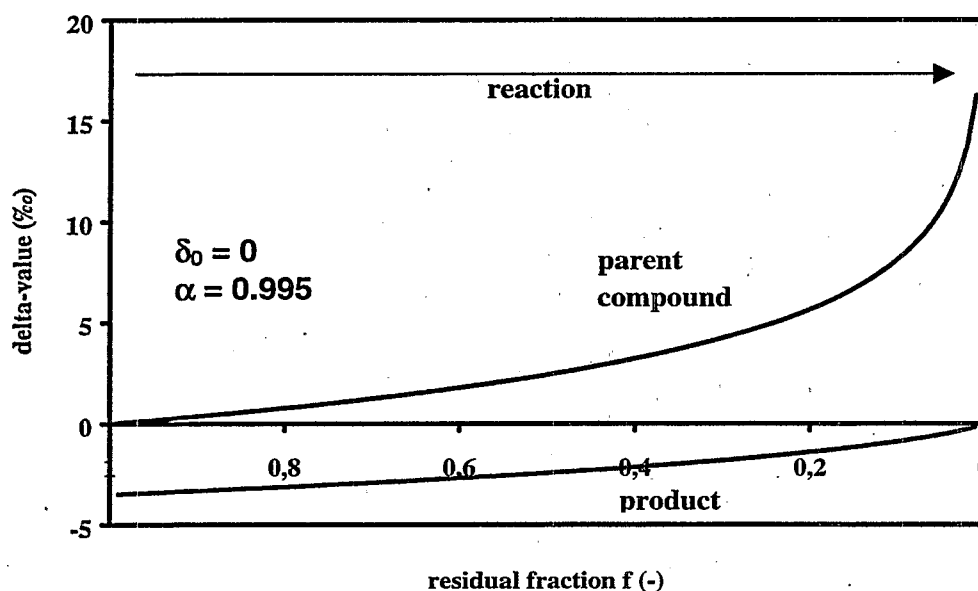
$$\delta^{13}\text{C} = \left(\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}}} - 1 \right) \times 1000 \quad (\text{‰ VPDB})$$

Due to difference in mass and size, stable isotopes of one element behave slightly different in many physical, chemical and biological processes. In most biodegradation processes, the lightest isotope is degraded preferentially. This causes a small, but usually significant change in the isotope composition of the residual pollutant. This so-called isotopic fractionation can be described with the Rayleigh equation:

$$R = R_0 \times f^{(\alpha-1)}$$

in which R is the isotope ratio (e.g. $^{13}\text{C}/^{12}\text{C}$), R_0 is the initial isotope ratio, f is the fraction residual substrate, and α is the fractionation factor. Figure 1 gives a theoretical example of the changes in isotopic composition (expressed as δ) of the parent compound (the pollutant) and the reaction product during a fractionating reaction.

Figure 1: Theoretical change in the stable isotope composition of reactant (parent compound) and reaction product during a fractionating reaction.



3. COMPOUND-SPECIFIC ISOTOPE ANALYSIS OF POLLUTANTS

Combination of a chromatographical pretreatment to separate different compounds with continuous flow isotope ratio mass spectrometry makes it possible to measure the stable isotope composition of individual organic components in a mixture. This so-called compound-specific stable isotope analysis (CSIA) allows us to determine the isotopic composition of a single organic pollutant in groundwater. For carbon, this technique has already been applied since 1997. Recently, CSIA of deuterium (^2H) has also become available. In the near future, CSIA is expected to become applicable to other relevant isotopes.

CSIA enables us to follow the isotopic composition of a pollutant during the course of biodegradation processes (parent compound in Figure 1). Laboratory studies have shown a strong isotopic fractionation of ^{13}C to occur during reductive and oxidative degradation of many chlorinated aliphatic hydrocarbons.

(e.g. PCE, TCE, DCE, VC, TCA, and DCA). For the degradation of aromatic hydrocarbons (BTEX, phenols) and MTBE, a small but significant ^{13}C -fractionation has been observed. Fractionation of ^2H has only been measured in a limited number of studies, but promises to offer very powerful evidence for biodegradation.

A literature example of the ^{13}C -fractionation during the reductive dechlorination of trichloroethylene (TCE) and the oxidation of 1,2 dichloroethane (DCA) is given in Figure 2 below. Table 2 presents a qualitative overview of the fractionation during different degradation processes, based on fractionation factors reported in the literature (laboratory studies).

Figure 2: Fractionating effect of trichloroethene (TCE) reduction and 1,2 dichloroethane (DCA) oxidation. TCE data from Sherwood-Lollar, et al., 1999; DCA data from Hunkeler and Aravena, 2000.

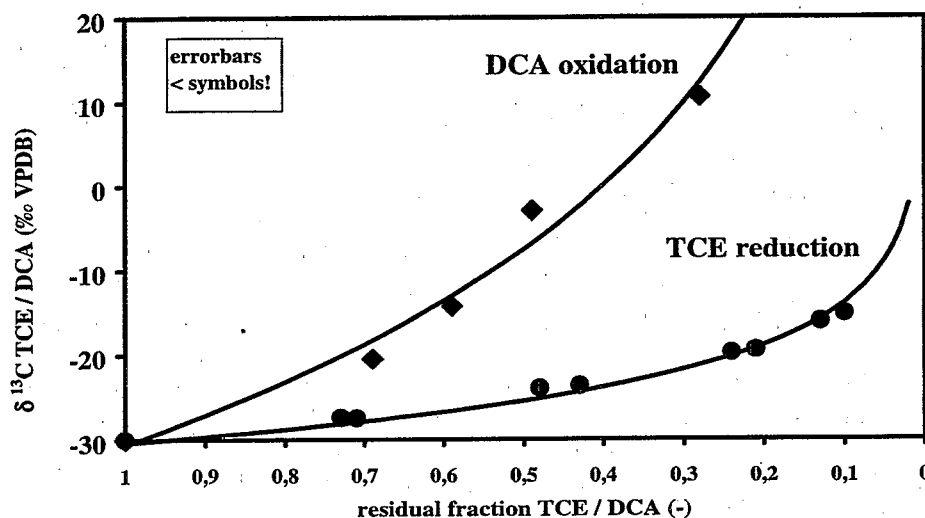


Table 3: Qualitative data on fractionation during different degradation processes.

Pollutant	Isotopic fractionation		
	Hydrogen	Carbon	Chlorine
chlorinated aliphatic hydrocarbons anaerobic			
tetrachloroethylene	n.a.	ooo	oo
trichloroethylene	oooo	ooo	oo
cis-dichloroethylene	?	ooo	?
vinyl chloride	?	oooo	?
chlorinated aliphatic hydrocarbons aerobic			
cis-dichloroethylene	?	oooo	?
dichloromethane	?	oooo	oo
aromatic hydrocarbons anaerobic			
benzene	ooo	o	n.a.
toluene	ooo	o	n.a.
ethylbenzene	ooo	o	n.a.
xylene	?	o	n.a.
miscellaneous hydrocarbons			
MTBE (aerobic)	ooo	oo	n.a.

NOTES:

o = limited fractionation
 ooo = strong fractionation
 n.a. = not applicable

oo = fractionation
 oooo = very strong fractionation

4. FIELD APPLICATION

To be able to use isotopic fractionation as evidence for biodegradation, it is essential to exclude fractionation by other processes. Of the processes occurring in groundwater, only volatilization and chemical transformation may have a significant fractionating effect. Other processes, such as dissolution, transport of solute molecules and sorption, do not affect the isotopic composition of pollutants significantly. Unexpectedly, volatilization seems to reduce the ^{13}C -content of volatile organic compounds and thus has a fractionating effect contrary to that of biodegradation. Therefore, isotopic enrichment of the residual pollutant provides conclusive evidence for in situ (bio)degradation.

CSIA can be applied in two different strategies. In the first strategy, CSIA is performed on contaminated groundwater samples along the source-plume path from one sampling round. Assuming degradation to proceed with transport of pollutant from the source zone, a sort of fractionation curve as presented in Figure 1 can be constructed by plotting the isotopic composition against the pollutant concentration. It should be noted that this is not a true fractionation curve, since the disappearance of pollutant will at least be partly caused by dilution. An alternative way of presenting the data is to plot the isotopic composition against the distance from the source zone. Using the source-plume strategy, it should theoretically be possible to use a known fractionation factor to calculate the extent of biodegradation that has occurred. As yet, however, our knowledge of isotopic fractionation is too limited to allow translation of fractionation factors obtained in laboratory experiments to the field situation.

The second strategy in which CSIA can be used is to include the analysis in a monitoring series. For analytical reasons, comparison of δ -values is best done within one measurement series. This implies that time-series of isotopic data from single monitoring wells are likely to have limited value. However, the comparison of isotopic trends within different sampling rounds can be very useful and can be used to provide evidence for ongoing biodegradation and to correct for seasonal fluctuations in pollutant concentrations.

4.1 Fractionation of Chlorinated Aliphatic Hydrocarbons

As can be seen in Table 3, the reductive and oxidative degradation of chlorinated hydrocarbons have a strong fractionating effect on both ^{13}C and ^2H . Therefore, CSIA is a good method for obtaining evidence for these degradation processes. However, the formation of less chlorinated intermediates during reductive dechlorination provides straightforward and conclusive evidence for degradation, diminishing the need for a more advanced technique such as isotope analysis. In complex cases with several source zones or with several different CAH present, additional evidence may be necessary. Recent field studies have shown CSIA of ^{13}C in PCE and TCE to be an effective characterization method (Sherwood Lollar et al. 2001).

4.2 Fractionation of Aromatic Hydrocarbons

With traditional techniques, it is very hard to obtain evidence for the (an)aerobic degradation of individual aromatic hydrocarbons in a mixture. Therefore, CSIA offers unique possibilities for aromatic hydrocarbons.

The source-plume strategy described above was applied in a recent research project at the site of Dow Benelux NV, Terneuzen, and The Netherlands. In this study, CSIA of both ^{13}C and ^2H have been used to investigate the natural attenuation of a contamination with benzene and ethylbenzene in an anaerobic aquifer (Mancini et al., 2001). From previous groundwater investigations, including a geochemical groundwater characterization, degradation of ethylbenzene was concluded to occur. Degradation of benzene, however, could not be ascertained. The results of the CSIA study are shown in the Figures 3 and 4 below.

Figure 3: Stable isotope composition (^{13}C , ^2H) of ethylbenzene in samples from the source zone (■) and the contaminant plume (◆).

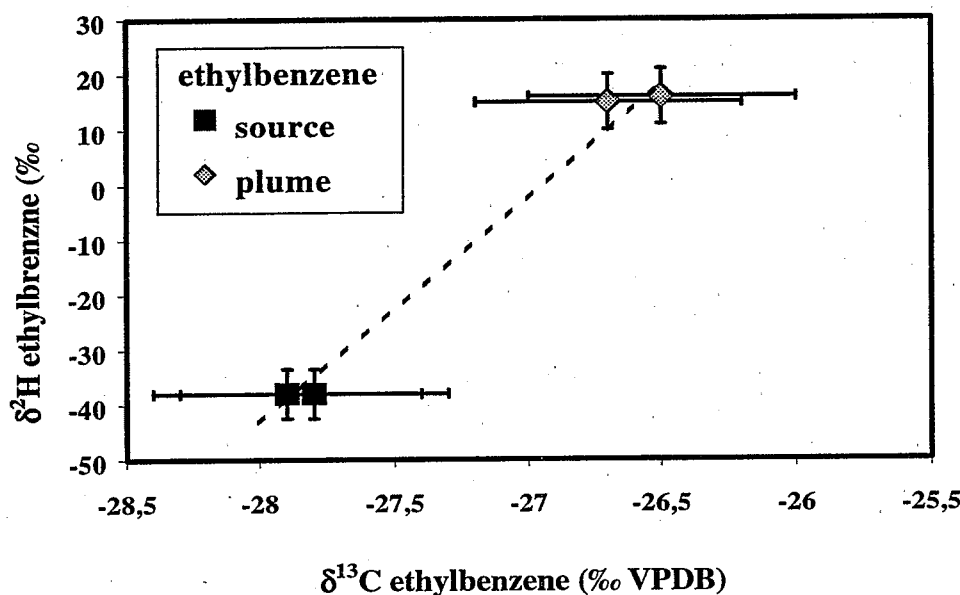
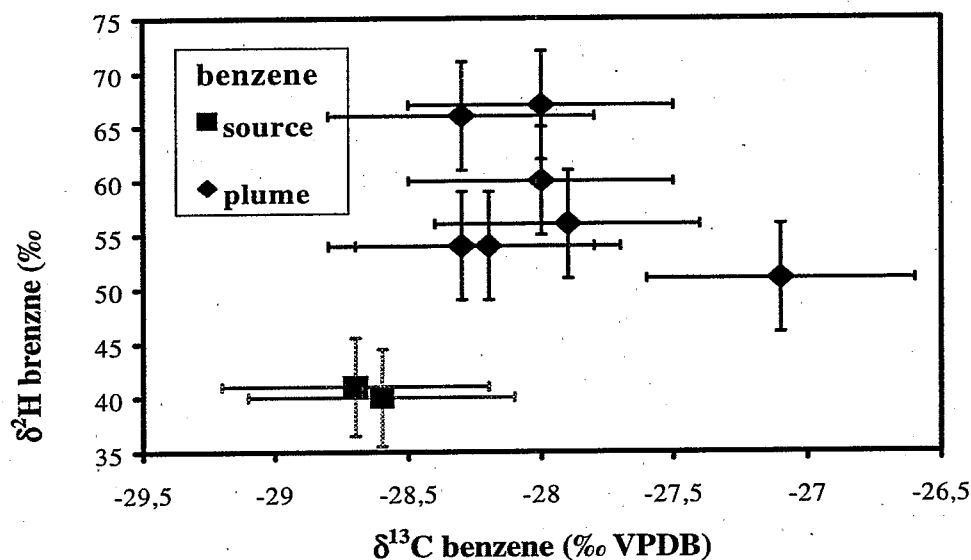


Figure 4: Stable isotope composition (^{13}C , ^2H) of benzene in samples from the source zone (■) and the contaminant plume (◆).



For both ethylbenzene and benzene, the data showed a small enrichment of ^{13}C (1-2‰) in samples from the plume compared to samples from the source zone. However, for the isotopic shift to become significant, a concentration reduction of approximately 80-90% was required. This need for samples in which degradation is in an advanced stage limits the applicability of ^{13}C CSIA. Therefore, the study also included CSIA of ^2H in ethylbenzene and benzene. The ^2H results showed a much stronger fractionating effect (fractionation of up to 60‰ for ethylbenzene and up to 28‰ for benzene) and provided conclusive evidence for the biodegradation of benzene, even in downgradient samples that still have relatively high pollutant concentrations. To our knowledge this is the first time field evidence for anaerobic degradation of benzene is obtained without the use of microcosm studies.

5. CONCLUSIONS

CSIA presents a new and very promising line of evidence for in-situ biodegradation. It has several advantages over existing methods in terms of specificity, conclusiveness, and cost-effectiveness. At present, CSIA is especially useful for degradation processes for which no other conclusive lines of evidence exist, such as the anaerobic degradation of benzene in a BTEX pollution. For other degradation processes, such as the reductive dechlorination of CAH, CSIA may be useful in complex situations or as an independent alternative line of evidence.

The practical application of CSIA in field studies is rather straightforward. Standard techniques can be used for groundwater sampling, and after a simple conservation step, samples can be sent to a specialized isotope laboratory. The most crucial steps in the process are the selection of the samples and the interpretation of the results.

CSIA still has some drawbacks, such as the limited number of laboratories able to perform the analyses, the high detection limits, the rather long turnover times and the relatively high analysis costs (especially for elements other than carbon). However, compound-specific isotope analysis is a rapidly developing technique, and it is expected that most of these drawbacks will be overcome soon.

6. ACKNOWLEDGEMENTS

The results presented here are obtained in a research project that was partly financed by the Dutch Soil Research Program (SKB), by Dow Benelux nv, and by the Dutch provinces of Drenthe, Gelderland, and Noord-Brabant.

Compound-specific isotope analyses of ^{13}C and ^2H for the study at the site of Dow Benelux NV, Terneuzen have been performed by Silvia Mancini from the Stable Isotope Laboratory of the University of Toronto.

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8. PRESENTATION VISUALS ~ presented by Frank Volkering

NATO/CCMS Pilot Project Phase III
Performance Verification of In Situ Remediation

Compound-specific stable isotope analysis

a new line of evidence for in situ bioremediation

Frank Volkering
Tauw bv, The Netherlands

Tauw

Evidence for bioremediation (1)

Ideal evidence:

- conclusive
- pollutants specific
- quantitative
- easy to obtain
- fast
- cost-effective (cheap)

Tauw

Evidence for bioremediation (2)

Traditional validation techniques

- Determination of nutrient concentrations
- Determination of soil moisture, temperature, permeability, etc. for mass flux and degradation studies
- not conclusive
- Genotoxicity and activity characterization
- not conclusive
- Microcosm or mesocosm experiments
- not conclusive

Tauw

Evidence for bioremediation (3)

New techniques

- biodegradation characterization
- not conclusive
- easy application
- easy to obtain
- fast
- cost-effective
- Hydrogen isotope analysis
- Carbon isotope analysis
- Compound-specific Stable Isotope Analysis (CSIA)

Tauw

ISOTOPE THEORY

Tauw

Elements and isotopes

- Atomic number = number of protons defines the element
- mass number = number of protons + number of neutrons defines the isotope
- Example:
 - 6 protons = 6 electrons = carbon
 - 6 neutrons = isotope 12 (carbon 12)
 - 7 neutrons = isotope 13 (carbon 13)
 - 8 neutrons = isotope 14 (carbon 14)

Tauw

Two types of isotopes

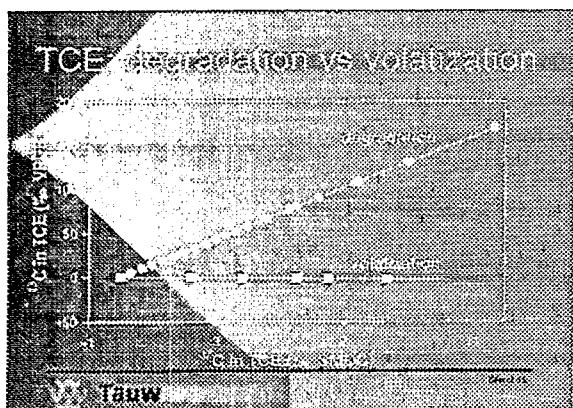
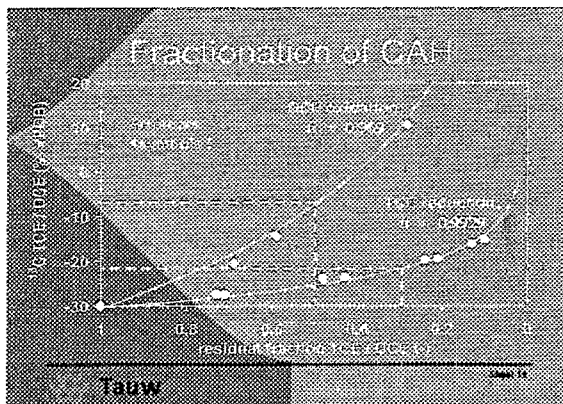
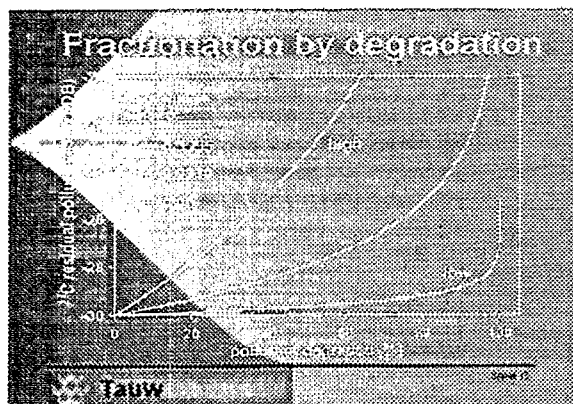
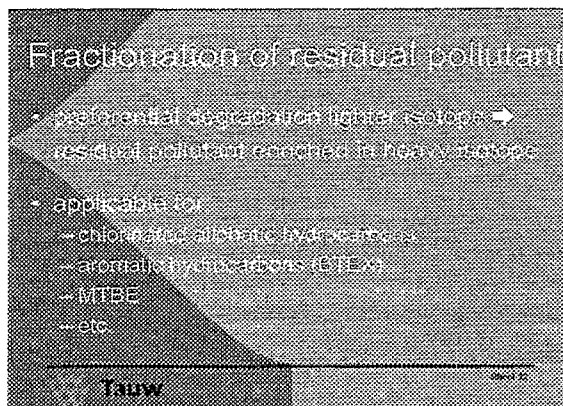
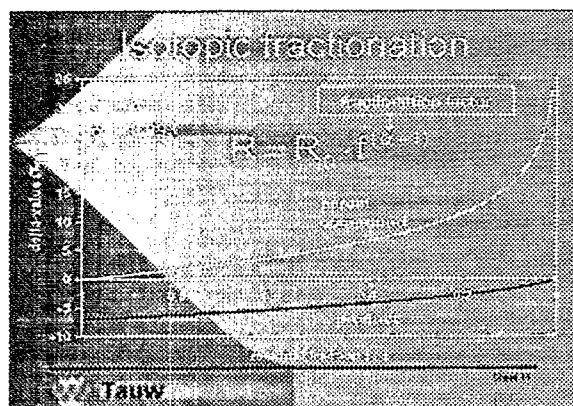
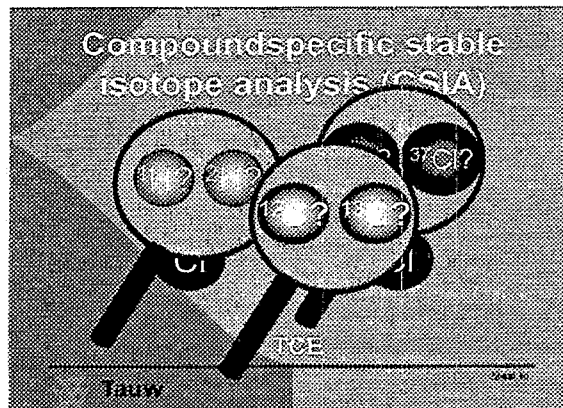
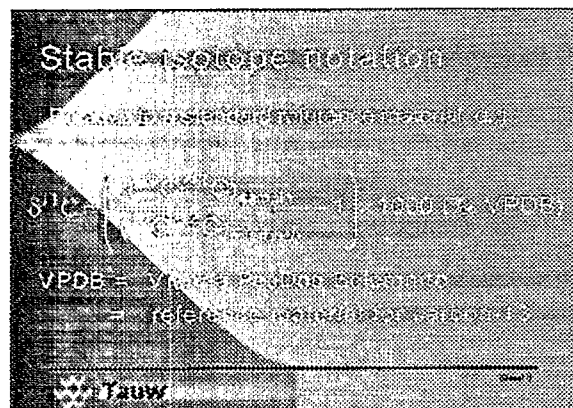
- 1 Radioactive isotopes (unstable)
 - emit alpha, beta, gamma radiation
 - half-life
 - used for dating
- 2 Stable isotopes (stable)
 - most abundant in nature
 - behave differently in chemical reactions (fractionation)

Tauw

Environmental isotopes

Isotope	Symbol	Atomic Number (Z)	Mass Number (A)	Relative Abundance (%)	Half-life (years)
Hydrogen-1	^1_1H	1	1	99.985	Stable
Hydrogen-2	^2_1H	1	2	0.015	Stable
Carbon-12	$^{12}_6\text{C}$	6	12	98.9	Stable
Carbon-13	$^{13}_6\text{C}$	6	13	1.1	Stable
Carbon-14	$^{14}_6\text{C}$	6	14	Trace	5730
Nitrogen-14	$^{14}_7\text{N}$	7	14	99.6	Stable
Nitrogen-15	$^{15}_7\text{N}$	7	15	0.4	Stable
Oxygen-16	$^{16}_8\text{O}$	8	16	99.76	Stable
Oxygen-17	$^{17}_8\text{O}$	8	17	0.04	Stable
Oxygen-18	$^{18}_8\text{O}$	8	18	0.2	Stable
Sulfur-32	$^{32}_{16}\text{S}$	16	32	95.0	Stable
Sulfur-34	$^{34}_{16}\text{S}$	16	34	4.2	Stable
Sulfur-36	$^{36}_{16}\text{S}$	16	36	0.02	Stable
Sulfur-38	$^{38}_{16}\text{S}$	16	38	Trace	Stable

Tauw



Two strategies

- CSA along source - plume path
 - evidence for anaerobic degradation
 - quantification of biodegradation (tauw)
- Including CSA in monitoring
 - evidence for anaerobic degradation
 - correction for geochemical speculations

Tauw

Slide 11

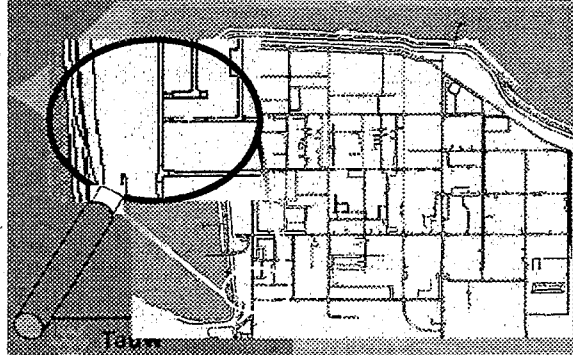
Isotopic evidence for the anaerobic degradation of benzene and ethylbenzene

Results of a field study at the site of Dow Benelux Terneuzen

Tauw

Slide 12

Dow Benelux site, Terneuzen



Tauw

Slide 13

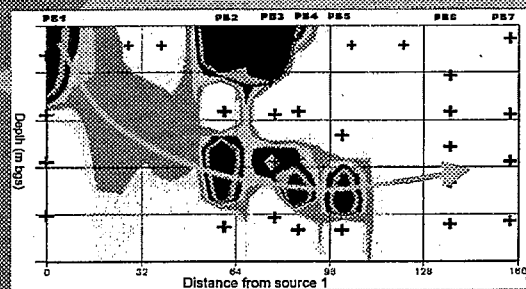
Site description

- Contamination with benzene and ethylbenzene
- Two source zones
- Plume length: benzene > 100 m
- Anaerobic groundwater (sulfate reducing / methanogenic)

Tauw

Slide 14

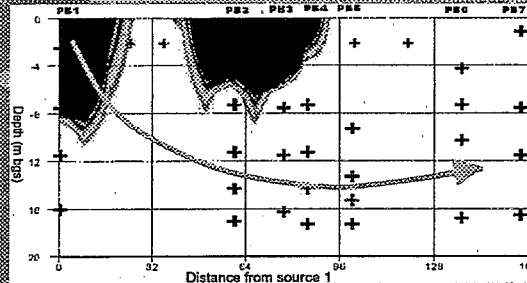
Cross section benzene



Tauw

Slide 15

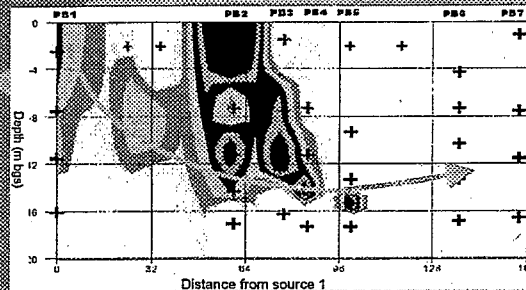
Cross section ethylbenzene



Tauw

Slide 16

Cross section methane



Tauw

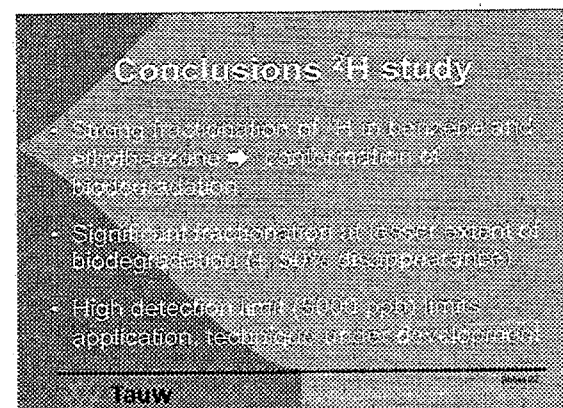
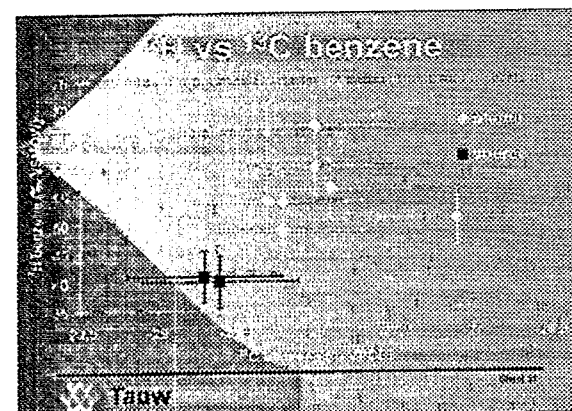
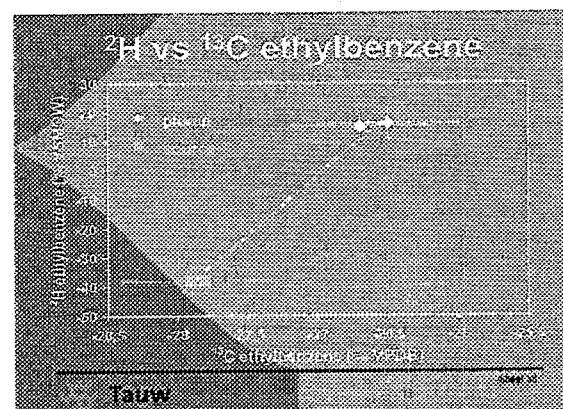
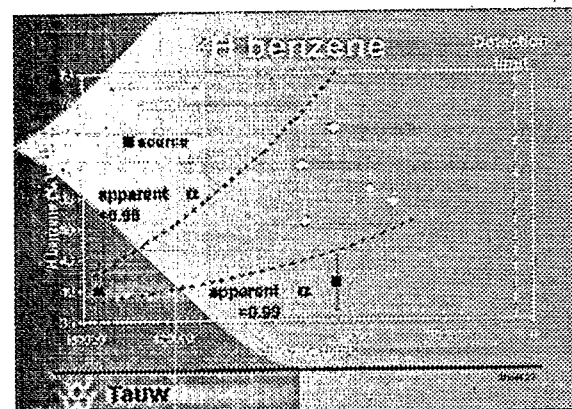
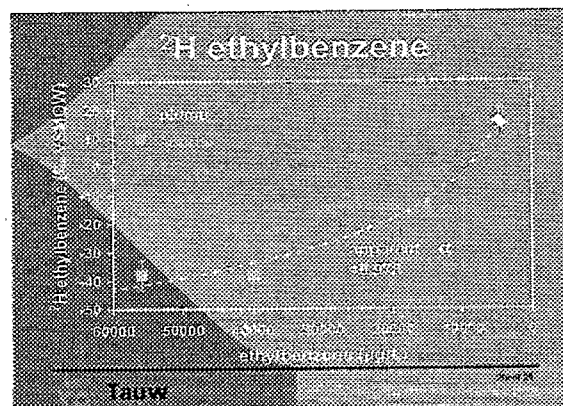
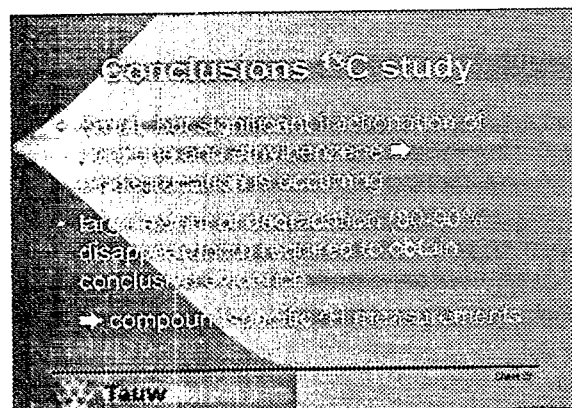
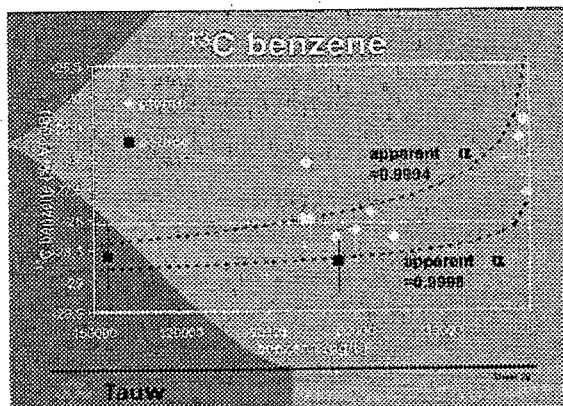
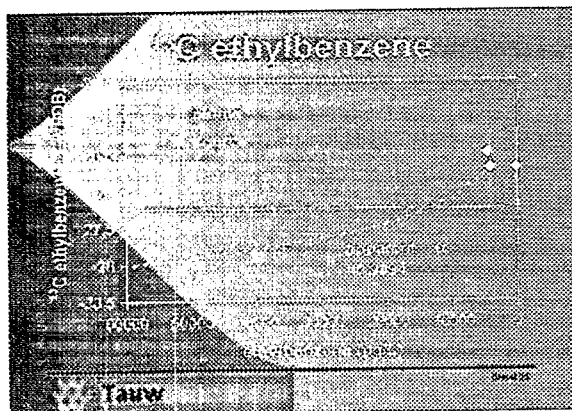
Slide 17

Conclusions "standard" NA study

- Sufficient evidence for anaerobic (methanogenic) degradation of ethylbenzene
- Anaerobic degradation of benzene: ???
- Additional information required
 - ➔ compound-specific ^{13}C analysis

Tauw

Slide 18



Practical aspects of CSIA

- Groundwater sampling & standards techniques
- Analysis: specialized techniques

Isotope	Status	Costs (USD)
^{13}C	Standard	25 - 250
^2H	Low	1
^{37}Cl	Not standard	high
O, N	Developing	?

Tauw

Slide 27

Applicability CSIA

Compound	analytical	reversibility
BTEX	C: fair H: high	high
CAH	C: high	moderate
MTBE	C: fair H: high	high

Tauw

Slide 28

Acknowledgements

- Erik Jonker, Sjoen and Grooten, Kees Groen (Vrije Universiteit Amsterdam)
- Silvia Madoni, Barbara Sherwood-Lollar (University of Toronto)
- SKB for funding

Tauw

Slide 29

Interested in isotopes?

Attend the symposium

"Natural isotope analysis in soil and groundwater pollution research"

October 10, Amsterdam

Tauw

Slide 30

For everything you always wanted to know about isotopes and more

State-of-the-art on isotope analysis

(available soon)

Tauw

Slide 31

Chlorinated hydrocarbons

- strong fractionation of ^{12}C and ^2H
- applicable for reductive dechlorination and oxidative degradation
- suited as second line of evidence besides intermediate formation

Tauw

Slide 32

Fractionation of TCE



Tauw

Slide 33

SITE-SPECIFIC VERIFICATION OF IN SITU CHEMICAL OXIDATION

Eric Hood¹, Robert L. Siegrist² and Neil Thomson³

1. INTRODUCTION

During the 1990's, in situ chemical oxidation (ISCO) emerged as a promising method for remediation of contaminated sites. As a site remediation technology, the goal of ISCO has been to destroy target organic chemicals present in soil and groundwater systems and thereby reduce the mass, mobility, and/or toxicity of contamination. Fundamental and applied laboratory research has elucidated many aspects of the reaction stoichiometry, degradation pathways, and kinetics for common organic chemicals in aqueous systems as well as the effects of temperature, pH, and matrix composition. Laboratory research has also explored the transport processes affecting oxidant delivery and dispersal in a porous medium like soil or aquifer sediments. Pilot-scale demonstrations and full-scale applications have attempted *in situ* treatment of aqueous and sorbed phase levels of organic contaminants, and to a lesser degree, dense nonaqueous phase liquids (DNAPLs). Oxidant delivery and distribution in the subsurface has been accomplished using injection probes, deep soil mixing, hydraulic fracturing, and vertical or horizontal groundwater wells. The literature now contains numerous research articles and technical reports, as well as several recent guidance documents that describe ISCO using hydrogen peroxide (or Fenton's reagent), ozone, and permanganate for treatment of organics in soil and ground water (e.g., USEPA 1998b, ESTCP 1999, Yin and Allen 1999, Siegrist *et al.* 2000, Siegrist *et al.* 2001).

Chlorinated solvents (as DNAPLs) are frequently released into the subsurface environment from industrial sources through both intentional disposal, and accidental leaks and spills. The United States Environmental Protection Agency (USEPA) reported in 1997 that DNAPLs may be present at up to 60% of the Superfund National Priorities List (NPL) sites (USEPA 1997). Of the 622 NPL sites reported in 1996, the chlorinated solvents trichloroethene (TCE) and perchloroethene (PCE) were detected in groundwater at 336 and 167 of these sites, respectively (USEPA 1998a). TCE and PCE are of particular concern because of the potential risks that they pose to human health; accordingly, the concentrations of these compounds have stringent regulatory levels.

At many sites, attempts to manage groundwater contamination associated with the presence of DNAPLs have met with limited success. The depth and areal distribution of DNAPLs often precludes any attempts at excavation while the effectiveness of pump-and-treat is limited by the low solubility of these contaminants, the weakness of dispersive mixing processes, and mass transfer limitations from the DNAPL into the dissolved phase. Increasingly, source removal technologies such as in situ chemical oxidation are being aggressively employed to remove DNAPL mass and/or reduce the concentration of the target contaminants below regulatory criteria with little knowledge of the expected performance of this technology. Only a limited number of controlled field trials that provide an indication of ISCO performance at DNAPL sites have been reported in the literature.

Several oxidizing agents are commonly used for ISCO including Fenton's reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$), and permanganate (MnO_4^-) (USEPA 1998b, Gates-Anderson *et al.* 2001, Siegrist *et al.* 2001). Fenton's reagent and permanganate can rapidly mineralize both TCE and PCE to inorganic products including chloride and carbon dioxide. The rapid degradation reactions enhance the removal of the DNAPL by increasing the concentration gradient that drives the rate of mass transfer. However, this technology is limited by the ability to advectively deliver the active oxidant (hydroxyl radicals in the case of Fenton's reagent) to the DNAPL in the subsurface. Oxidant delivery is complicated by both geologic heterogeneity and secondary oxidation reactions between the reagent and the reduced organic and inorganic phases within the natural aquifer matrix.

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A number of factors can limit DNAPL removal by ISCO. While the DNAPL mass present in regions of the aquifer where oxidant delivery is dominated by advection may be readily removed, the rate of mass transfer from DNAPL mass in stagnant zones is limited by diffusion of the contaminant and oxidant through the water surrounding the DNAPL. Oxidant delivery through diffusion and the degradation of TCE in low permeability zones has been demonstrated (Siegrist *et al.* 1999, Struse *et al.* 2001). However, oxidant delivery by diffusive transport alone is less likely to result in a significant mass transfer and degradation enhancement (Hood and Thomson 2000).

2. REMEDIATION EFFECTIVENESS

As observed in a controlled field trial evaluating the performance of ISCO using permanganate (Schnarr *et al.* 1998) the most optimistic result is complete DNAPL removal. Since the DNAPL resulting in the formation of a groundwater plume is removed, the concentration of the contaminant in groundwater will decrease over time and eventually should reach background levels.

The most likely outcome of an ISCO treatment approach at a DNAPL site, is partial DNAPL mass removal accompanied by a reduction in the average concentration of DNAPL organics in the groundwater plume. In the short-term, residual oxidant (e.g., permanganate) in the treatment zone following the period of active oxidant injection will continue to degrade dissolved phase compounds to non-detectable concentrations. However, as oxidant is flushed from the treatment zone by groundwater flow and/or reacts with naturally occurring reductants within the soil matrix, the DNAPL organic concentrations may increase, but remain at a level that is less than pre-treatment concentrations.

3. PERFORMANCE INDICATORS

Various criteria may be used to assess the performance of in situ remediation technologies such as ISCO. These performance indicators are described below, particularly as they apply to DNAPL sites.

3.1 Contaminant Mass

The total mass of DNAPL present at a site may be estimated through interpolation and extrapolation of the spatial distribution of contaminant concentrations in soil; however, this approach is complicated by the high degree of heterogeneity frequently observed in the distribution of DNAPL in natural geologic environments. The number of samples required to adequately estimate the DNAPL mass is sufficiently large that the costs of sample collection and analysis are prohibitive.

3.2 Groundwater Concentration

The most common performance assessment approach is the comparison of pre- and post-treatment volatile organic compound (VOC) concentrations in a network monitoring wells. In comparison to DNAPL mass, this approach more closely represents the exposure risks typically associated with groundwater contamination (i.e., direct ingestion of groundwater containing VOCs). As previously discussed, VOC concentrations in the monitoring wells measured immediately following the oxidant injection period are likely to be biased low due to the presence of residual oxidant in the treated zone. Further, the presence of any amount of DNAPL following ISCO will result in groundwater concentrations exceeding regulatory criteria since the solubility of these compounds is greater than the criteria by several orders of magnitude. As a result, monitoring wells located immediately adjacent to the remaining DNAPL may provide results that are biased high and are not reflective of the overall impact of ISCO treatment.

A number of potential limitations to this performance assessment approach should be considered during the design of a post-treatment monitoring program. Since residual oxidant will tend to negatively bias the post-treatment estimate of the average plume VOC concentrations, monitoring efforts should emphasize characterizing the long-term, steady-state VOC concentration in the monitoring network. Since the DNAPL remaining following treatment will result in local zones of high VOC concentrations that may

positively bias the average post-treatment plume concentration, the number of sampling points must be sufficiently large to reflect a representative spatially averaged VOC concentration.

3.3 Groundwater Flux

The ideal performance assessment criterion is the rate of mass removal (expressed as a flux multiplied by the DNAPL:water interfacial surface area) from the DNAPL source into the groundwater plume. At steady-state, this rate (termed the plume load with units of $M T^{-1}$), is equivalent to the rate at which solute mass in the groundwater plume crosses a spatial plane oriented at a right angle to the direction of groundwater flow. The plume load is distinguished from plume flux that is the rate of mass flow per unit area with units of $M T^{-1} L^{-2}$. In some sense, the collection of a sufficiently large number of samples randomly located within the groundwater plume will provide an adequate data set for determination of plume load; however, more cost-effective approaches may be employed to collect plume load data. In the simplest approach, steady-state VOC concentration data may be collected from an extraction well pumped at a continuous rate that is sufficient to create a steady-state capture zone that encompasses the entire groundwater plume. Using the flow rate and average VOC concentration, the plume load may be directly calculated. While the time required to achieve a steady-state VOC concentration in the extraction well is a potential constraint, the ease of data collection makes this a potentially attractive approach. Alternatively, plume load may be determined using an approach made feasible by the advent of inexpensive multilevel sampling piezometers and drivepoint profiling tools. Using a closely spaced transect of groundwater samples from a plane intersecting the groundwater plume and oriented at a right angle to the direction of groundwater flow, the plume load may be calculated using an estimate of the Darcy velocity and spatial interpolation of the concentration distribution across the sampling transect. While requiring complex data interpolation and relatively high sample collection and analysis costs, this approach is rapid in comparison to continuous pumping from an extraction well.

4. FIELD APPLICATIONS

4.1 Features and Performance Observations

Field applications of ISCO are growing rapidly in the U.S. and abroad as highlighted in recent articles and reports (e.g., Jerome *et al.* 1997, Schnarr *et al.* 1998, ESTCP 1999, Lowe *et al.* 2001, USEPA 1998b, Siegrist *et al.* 1999, Yin and Allen 1999, Siegrist *et al.* 2001). In general, ISCO systems have been shown to be capable of achieving high treatment efficiencies (e.g., >90 to 99%) for common COCs such as chlorinated ethenes (e.g., TCE, PCE) and aromatic compounds (e.g., benzene, phenols, naphthalene), with very fast reaction rates (e.g., >90% destruction in minutes). Field applications have demonstrated that ISCO can achieve destruction of COCs and achieve clean-up goals at some contaminated sites. However, field-scale applications can also have uncertain or poor in situ treatment performance. Uncertain or poor performance is often attributed to poor uniformity of oxidant delivery caused by low permeability zones and site heterogeneity, excessive oxidant consumption by natural subsurface materials, presence of large DNAPL masses, and incomplete degradation. Assessment of treatment efficiency is commonly based on sampling and analysis of soil and/or groundwater to enable comparison of post-treatment concentrations to those present prior to ISCO. These approaches are fraught with problems due to heterogeneities in the subsurface and the limited number of samples from which inferences are to be made. In addition, simply characterizing the treated region may not provide the proper information regarding performance as it does not specifically address changes in contaminant flux that may result from partial cleanup of a source zone feeding a plume. The following case study illustrates alternative performance assessment approaches as evaluated during a field trial.

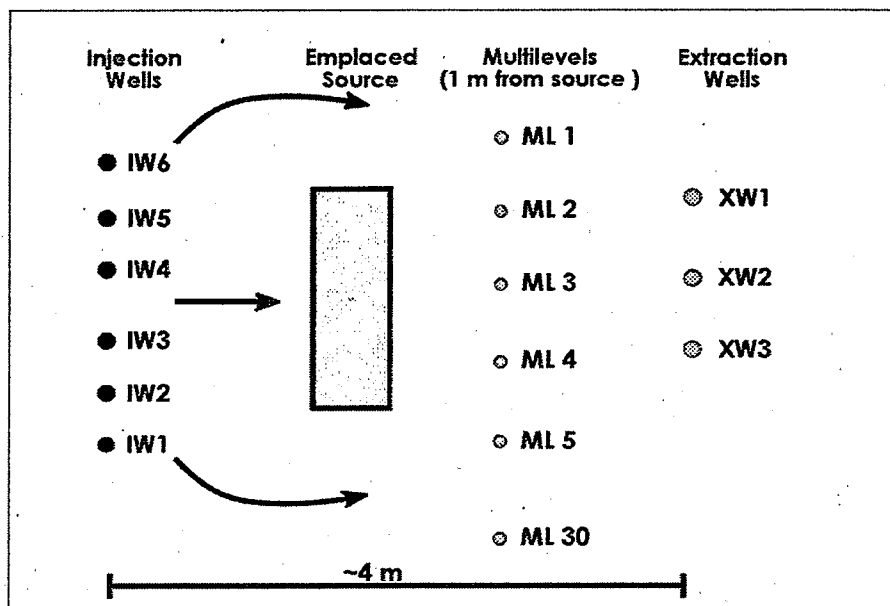
4.2 Case Study Illustrating Performance Assessment Approaches

A pilot demonstration of ISCO using permanganate was conducted in a shallow sandy aquifer (Hood *et al.* 2000). The DNAPL source zone consisted of mixture of TCE and PCE as a residual; the dimensions of the source zone were 1.5 m x 1.0 m x 0.5 m. The groundwater monitoring and oxidant delivery system consisted of six injection and three extraction wells, along with a fence of multilevel piezometers

containing sample points spaced ~0.5 m horizontally and 0.2 m vertically (Figure 1). The DNAPL source was flushed with potassium permanganate at a concentration of 8 g/L for 480 days.

The performance assessment approach at the demonstration site utilized a comparison of the three indicators previously described (DNAPL mass, peak plume concentration, and plume load). DNAPL mass reduction was based on pre-treatment DNAPL mass estimated using a modeling approach and post-treatment soil sampling (>300 samples). Peak concentrations in the pre- and post-treatment groundwater plume were measured as the maximum concentration detected from the multilevel transect. The spatial distribution of VOC concentrations in the multilevel transect was used to calculate pre- and post-treatment plume loads. In addition, the steady-state VOC concentrations in the extraction wells were used as a comparative plume load measurement.

Figure 1: Plan view of test site, including injection wells (IW), multilevel piezometers (ML), and extraction wells (XW). The shaded box represents the location of the DNAPL source zone.



The results of the performance assessment are summarized in Table 1. During post-treatment soil sampling, DNAPL was not detected in any of the soil samples and only a few detections of sorbed TCE or PCE were observed, suggesting that the DNAPL was entirely removed. In contrast, the peak plume concentrations of both TCE and PCE observed in the multilevel transect located immediately down-gradient of the source zone decreased by factors of only 70 and 2, respectively, relative to pre-treatment conditions. This relatively minor decrease was consistent with a positive bias in concentration resulting from the presence of DNAPL, in spite of the detailed soil sampling efforts suggesting the DNAPL was not present. In contrast to these contradictory results, the observed reductions in the TCE and PCE plume loads (decreased from the pre-treatment plume loads by approximate factors of 100 and 10, respectively) measured using both the transect and continuous extraction methods were consistent between measurement methods.

Table 1: Summary of chemical oxidation performance assessment data.

Performance Indicator	Pre-treatment (TCE/PCE)	Post-treatment (TCE/PCE)
DNAPL Mass (kg)	1.6 / 9.0	ND / ND
Peak Concentration (ug/L)	142 / 61	2 / 31
Transect Plume Load (mg/day)	836 / 854	7 / 98
Extraction Plume Load (mg/day)	2,099 / 2,218	17 / 222

ND = non-detectable.

5. SUMMARY

Short-term monitoring programs using a sparse monitoring network to assess the impact of in situ chemical oxidation on remediation performance can be inadequate and misleading. This is particularly true for DNAPL sources of groundwater contamination, where such approaches can be subject to either negative or positive bias. Design of such programs should focus on determining the post-treatment reduction achieved over a sufficiently long monitoring period so that residual oxidant does not interfere with the observed COC concentrations. In addition, assessments should rely on steady-state reductions observed in multiple monitoring wells within the former extent of the groundwater plume rather than reductions observed in a single monitoring point that could be easily biased. Plume flux is a valuable performance assessment tool, although its applicability at some industrial sites may be limited by the time and cost required to complete these measurements using rigorous methodologies.

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7. PRESENTATION VISUALS ~ presented by Robert L. Siegrist

**Site Specific Validation of
In Situ Chemical Oxidation
(ISCO)**

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NATO/CCMS Country Representatives Meeting
Liege, Belgium
9 - 14 September 2001

In Situ Chemical Oxidation

- In situ chemical oxidation (ISCO) involves "delivery of oxidants into the subsurface to destroy contaminants and reduce their concentrations and mass."
- During the early 1990's, research confirmed ISCO's potential viability for *in situ* remediation:
 - ✓ Use of H_2O_2 (Fenton's), O_3 , $KMnO_4$, $NaMnO_4$
 - ✓ For chlorinated solvents and petrochemicals
- To date, more than 200 field applications have occurred with subsurface delivery by:
 - ✓ Vertical & horizontal ground water wells
 - ✓ Injection probes, fracturing, soil mixing

Fenton's reagent via probe injection at MGP site in Wisconsin (Geo-Cleanse)

$KMnO_4$ via probe injection at a TCE DNAPL site in Florida (IT Group)

$NaMnO_4$ via 5-spot vertical wells at a dissolved phase TCE site in Ohio (ORNL)

Reactions with Organics

- Many organics of concern can be mineralized to CO_2 , water, salts and oxides, with possible intermediates
- Simplified oxidation stoichiometries for TCE (aqueous):

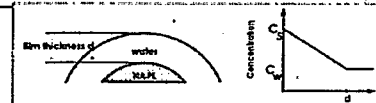
$$3H_2O_2 + C_2HCl_3 + Fe \rightarrow 2CO_2 + 2H_2O + 3H^+ + 3Cl^- + Fe$$

$$O_3 + H_2O + C_2HCl_3 \rightarrow 2CO_2 + 3H^+ + 3Cl^-$$

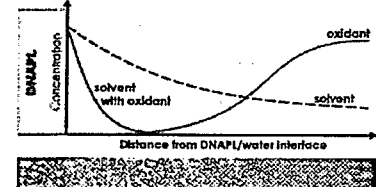
$$2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_2 + 2K^+ + H^+ + 3Cl^-$$
- Free-radical (Fenton's, O_3) or direct electron transfer processes (MnO_4^-) are involved
- NAPLs can be degraded by oxidation enhanced mass transfer and oxidative destruction

Reactions with DNAPLs

DNAPL dissolution into groundwater with no oxidant

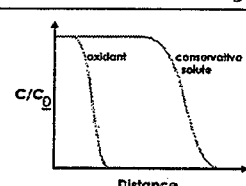


ISCO enhanced mass transfer and degradation



Reactions with Soil

- Natural oxidant demand (NOD) can be due to reduced substances in the subsurface such as:
 - ✓ Soil organic matter
 - ✓ S²⁻
 - ✓ Fe²⁺ and Mn²⁺

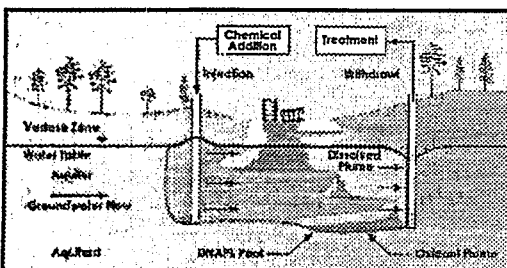


NOD can be significant as it affects oxidant delivery and treatment costs

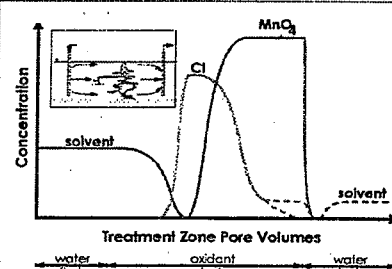
Sample	g/kg	\$/m ³
A	11.7	59
B	1.2	6

Subsurface Transport

Advective-dispersive and in some cases diffusive transport



Integration of Processes



Site-Specific Validation

Validation of ISCO performance goal achievement at a specific site can include:

- ☐ Soil and/or groundwater sampling to define:
 - ▲ Concentrations in soil and/or groundwater ($M L^{-3}$)
 - ▲ Contaminant mass before and after ISCO (M)
- ☐ Plume mass flux ($M T^{-1} L^{-1}$) or plume load ($M T^{-1}$)
- ☐ Estimates of total mass destruction (%)
- ☐ Toxicity assays (via bioassay methods)
- ☐ Other measures of ISCO function
 - ▲ Subsurface geophysical mapping
 - ▲ Soil/groundwater reaction byproducts (Cl⁻)
 - ▲ Soil/groundwater chemistry (oxidant, pH, Eh, D.O.,...)

Site-Specific Validation

Validation of ISCO performance goal achievement at a specific site normally can not include:

- ☐ Measurements of mass recovered as in mass recovery based methods
- ☐ At present, the use of multicomponent partitioning tracers is still under study

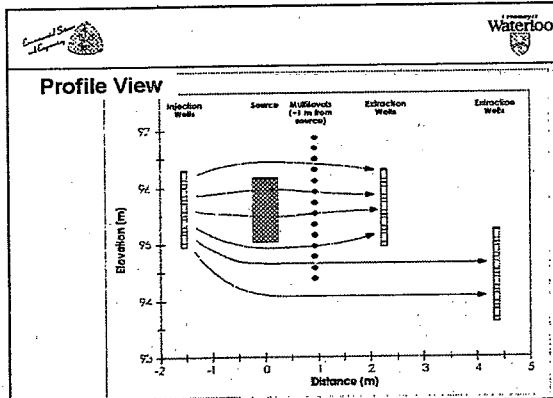
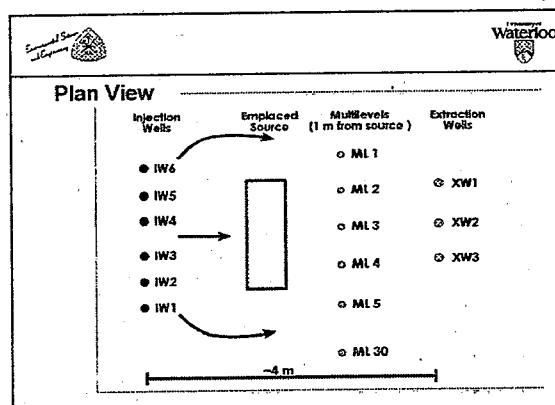
Examples

Field Trial in Canada

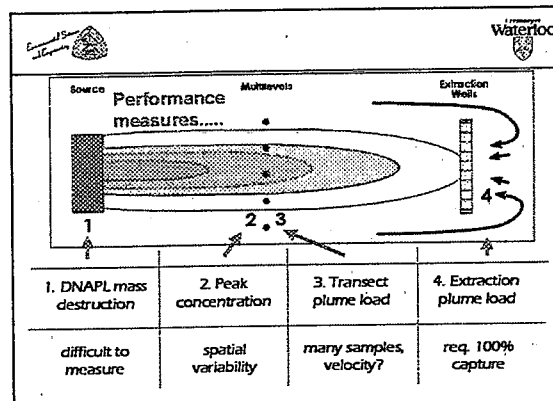
Application Description

- ✓ Well-characterized, homogeneous sand aquifer
- ✓ Residual DNAPL source zone containing TCE and PCE
- ✓ Highly instrumented
- ✓ ISCO using $KMnO_4$ in a horizontal flushing mode

Hood, 2000; Hood and Thomson, 2001



Operation mode	Objectives	Monitoring
Pre-oxidation water flush (75 days)	-characterize flow -plume load	VOCs, Br
Oxidant flush (484+177 days)	-remove DNAPL -monitor performance	Cl ⁻ , $KMnO_4$
Post-oxidation water flush (119 days)	-residence time -plume load	VOCs, Br
Source coring	-mass of DNAPL, MnO_2	VOCs, Mn



Results

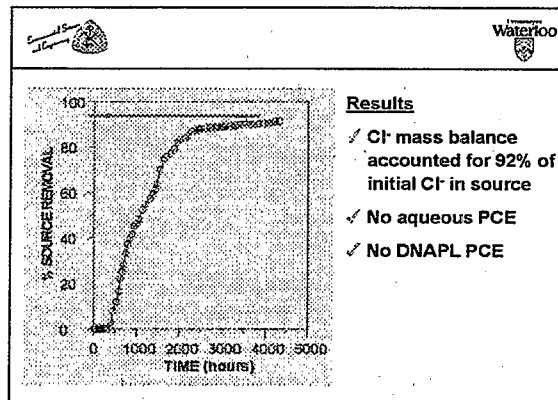
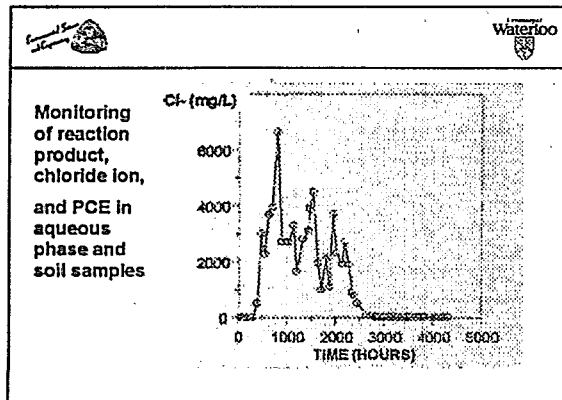
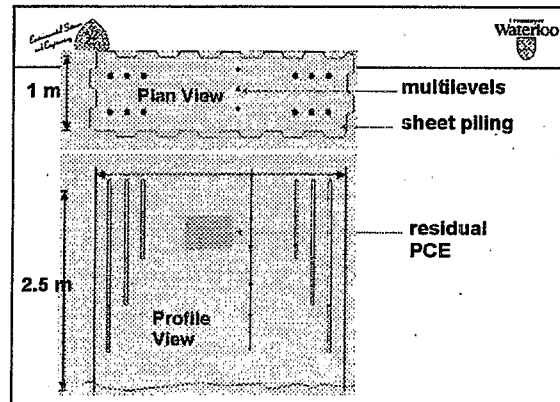
Measure	Pre-ISCO (TCE or PCE)	Post-ISCO (TCE or PCE)
DNAPL mass (kg)	1.6 / 9.0	ND / ND
Peak concentration (ug/L)	142 / 61	2 / 31
Transect plume load (mg/d)	836 / 854	7 / 98
Extraction plume load (mg/d)	2099 / 2218	17 / 222

CFB Borden Site in Canada

Application Features

- ✓ Closed system inside sheet pile cell
- ✓ 1.6 kg PCE, ~8% residual saturation
- ✓ Single pass with no oxidant recycling
- ✓ Flush with 10 g/L KMnO_4

MacKinnon and Thomson, 2001

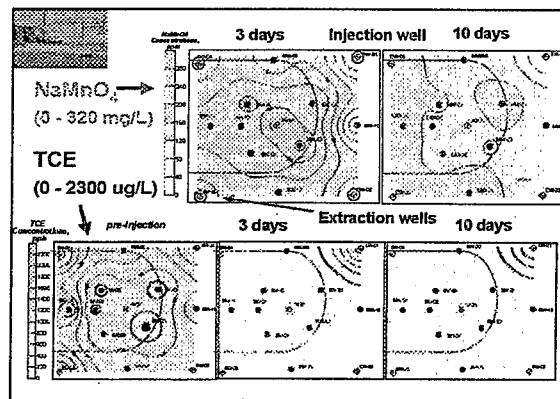


Field Site in Ohio

Application Features

- GW with TCE at 2,000 ug/L
- 5 spot pattern at 45 ft. radius from center injection
- GW extraction, 250 mg/L NaMnO_4 oxidant reinjection
- Sampling & analysis of 1 injection and 4 extraction wells, and 10 monitoring wells for TCE, reaction products, biotoxicity

Lowe et al., 2001; Siegrist et al., 2001



Results

- ✓ 97% overall treatment after 10 days as measured by a integrated decrease in concentrations and an estimated mass destruction
- ✓ No loss in formation Ksat
- ✓ No biotoxicity

MacKinnon and Thomson, 2001

Closing Remarks

- ✖ Chemical oxidation is an emerging technology for *in situ* remediation and its application is supported by process principles, R&D, and field experiences
- ✖ Validation of chemical oxidation at a specific site can currently utilize a combination of approaches to measure treatment effects on:
 - Contaminant concentrations (soil and groundwater)
 - Plume load (levels at monitoring & recovery wells)
 - Mass destruction (estimated from discrete samples)
 - Toxicity (e.g., bioassays)
 - Subsurface geophysics (e.g., oxidant) and biogeochemistry (e.g., reaction products)

MacKinnon and Thomson, 2001

SITE-SPECIFIC VERIFICATION OF IN SITU PERMIABLE REACTIVE BARRIERS

Volker Birke¹

1. THE FUNNEL & GATE SYSTEM AT EDENKOBEN

Setting-up and operating the full-scale funnel & gate system at Edenkoben

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Pollutants

Cause of contamination: solvents applied in production processes (automobile parts)

Av. of single HaloVOCs: 20% TCE, 50% cisDCE, 30% 1,1,1-TCA

At least 3 single plumes, partly overlapping:

- Plume South: TCE, cisDCE, $\leq 8.000 \mu\text{g/l}$ HaloVOCs
- Plume middle: 1,1,1-TCA, TCE, cisDCE, $\leq 20.000 \mu\text{g/l}$ HaloVOCs
- Plume North: PCE, $\approx 2.000 \mu\text{g/l}$ HaloVOCs

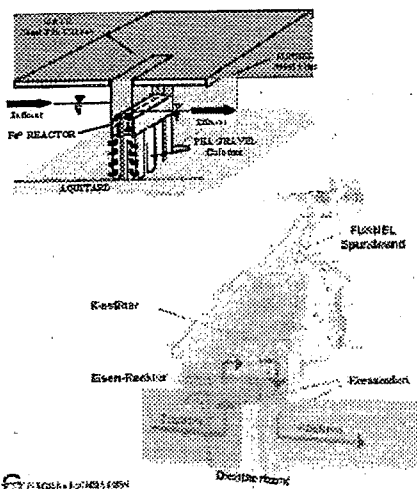


Figure 2 – Construction of the f & g system

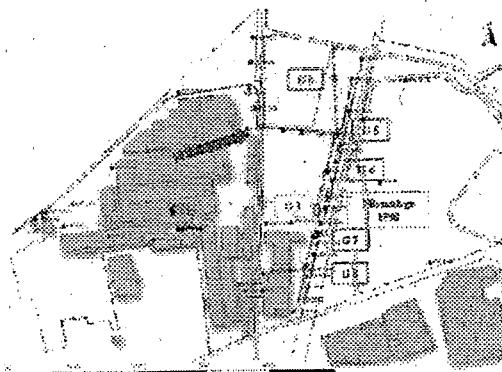


Figure 1 – Location of the existing funnel & gate system of the Edenkoben site

Wall System

Funnel & gate (vertical flow)

Depth of wall: appr. 15 m

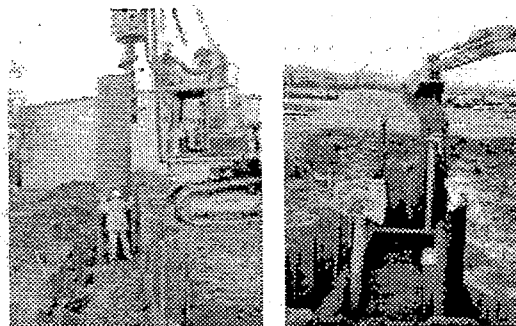
Reactive material: Fe^0 fillings

6 gates (each 10 m wide) surrounded by a sheet pile caisson (open towards the bottom), that covers appr. 8 m below ground level

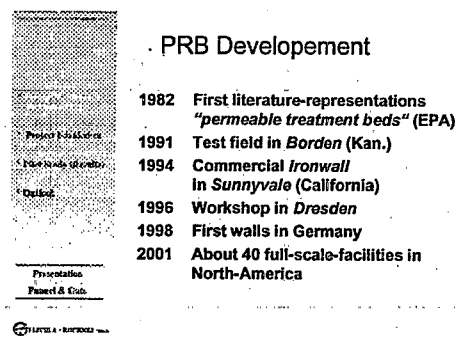
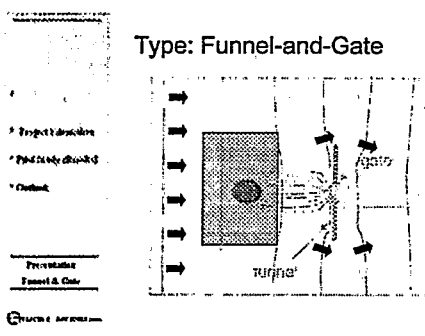
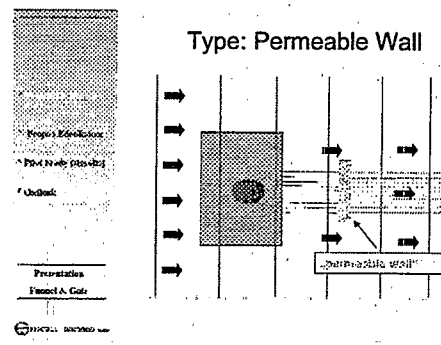
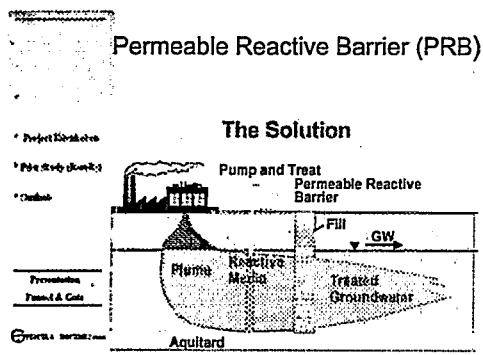
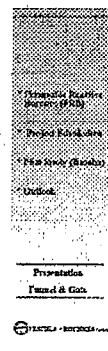
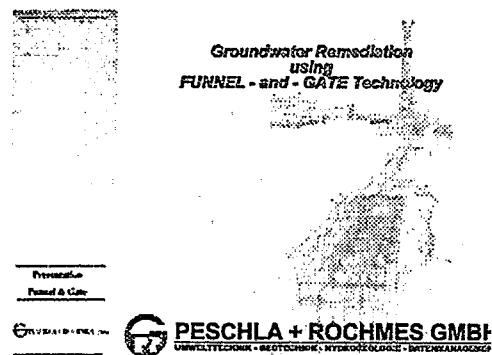
Continuous sheet pile wall, 400 m long (involves 14 m of below ground level into aquifer base), separating gates into two chambers (each 1,25 m wide); in the area of the gate the sheet pile wall was buried down to 1 m below the anticipated lowest GW level (at 5 m below ground level) serving as an overflow weir between the chambers (vertical flow, flow direction was intentionally lengthened by the reaction zone)

Outside of the gate, the wall in the middle reaches up to ground level forming the funnel

Complete connection of the deeper, polluted GW areas via vertical drainages

Figure 3 – Right photo: set-up of the vertical drainages using a large diameter borehole construction method; left photo: filling the gate with Fe^0 ¹ Kaiserslautern, Germany. www.gpr.de www.rubin-online.de

2. PRESENTATION VISUALS ~ presented by Volker Birke



Advantages of This Technology

- ❑ The location of the source has not to be known exactly, no requirement of direct access to the source zone
- ❑ Integral inclusion of the plume especially at heterogeneous and low permeable aquifers
- ❑ Low influence in the groundwater system
- ❑ Low consequences for infrastructure
- ❑ Reduced maintenance and low operating costs
- ❑ Cost advantages in longterm measures

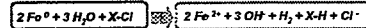
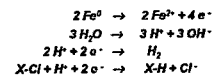
Risks of This Technology

- ❑ The hydrogeological situation has to be well known (placement, dimensioning)
- ❑ Critical in the case of increasing contamination rates
- ❑ Changes of the groundwater chemistry (pH, conductance)
- ❑ Low experience / knowledge about the longterm stability (inhibiting, precipitates)
- ❑ Source remains in the underground
- ❑ High investigation costs

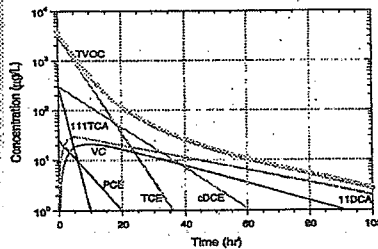
Iron Filings (Fe^0)



Metal enhanced dehalogenation



Degradation of VOCs



Case Study - Edenkobben

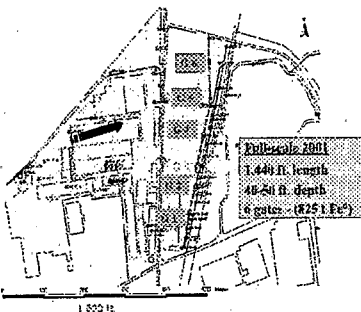
Site: Automotive Industrial Plant

Contaminants: VOCs (PCE, TCE, cDCE, 111TCA)

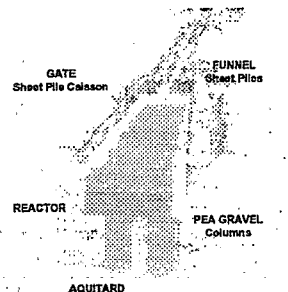
Constr. Type: Funnel-and-Gate
 Funnel: sealed sheet piles
 Gates: sheet pile caisson
 vertical flowthrough

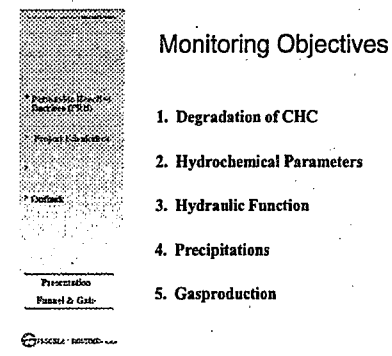
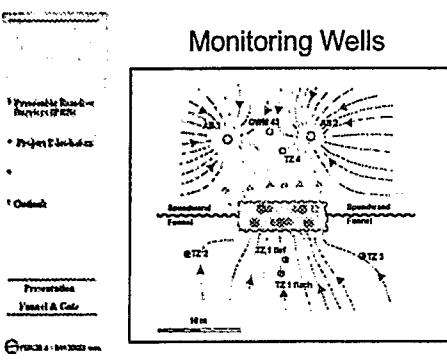
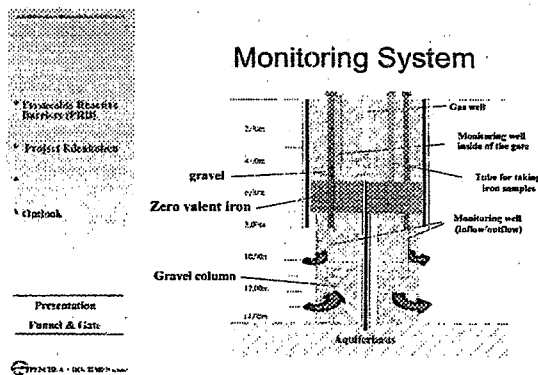
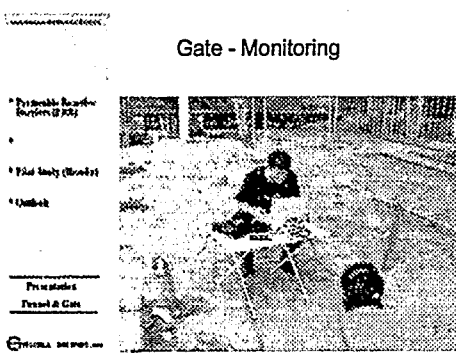
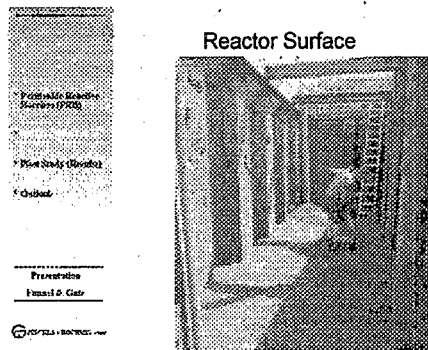
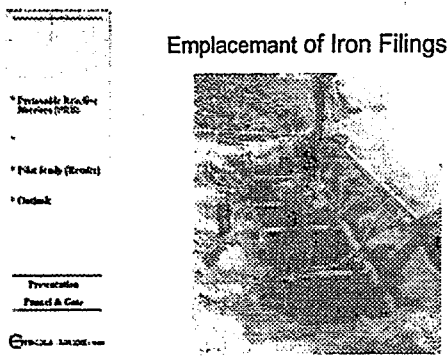
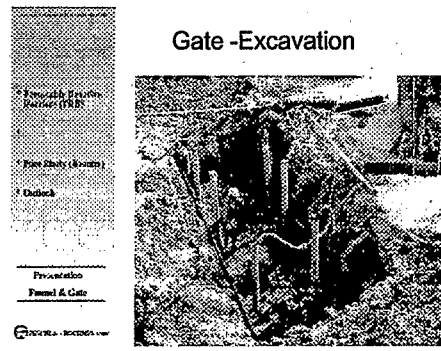
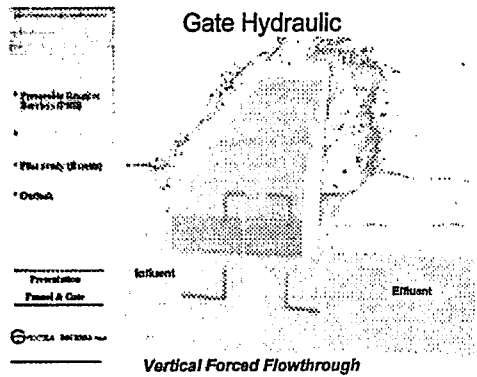
Reactive Media: Zero-Valent Iron

Edenkoben Site

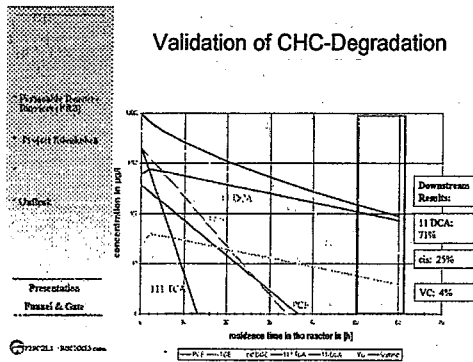


Gate-Construction





Validation of CHC-Degradation



Conclusions

- ☐ The targetted remediation values were reached and even exceeded
- ☐ > 98 % effectiveness rate
- ☐ No further obstructions on the site
- ☐ Low maintenance costs („passive system“)
- ☐ Monitoring - the future activity

Outlook

R & D Project of the German Federal Ministry for Education and Research ("BMBF")

"Applying Reactive Barriers and Treatment Zones in Germany"

- ☐ Duration: 3 years
- ☐ Financial scope: Approx 4 Mil Euro
- ☐ About 10 Projects
- ☐ 6 projects with zero valent iron

R & D Project

Issues that have to be addressed and clarified:

- Appropriate boundary conditions for GW-remediation using treatment walls?
- Advantages and limits of this remediation technology?

Detailed Objectives

- Gaining data from as different cases and applications as possible for assessing benefits, drawbacks and applicability of treatment walls
- Information on design, construction and operating
- Impact and benefits regarding the environment
- Testing of already installed treatment walls
- Reduction of pollutants pertaining to long-term aspects
- Rentability
- Developing and establishing quality standards

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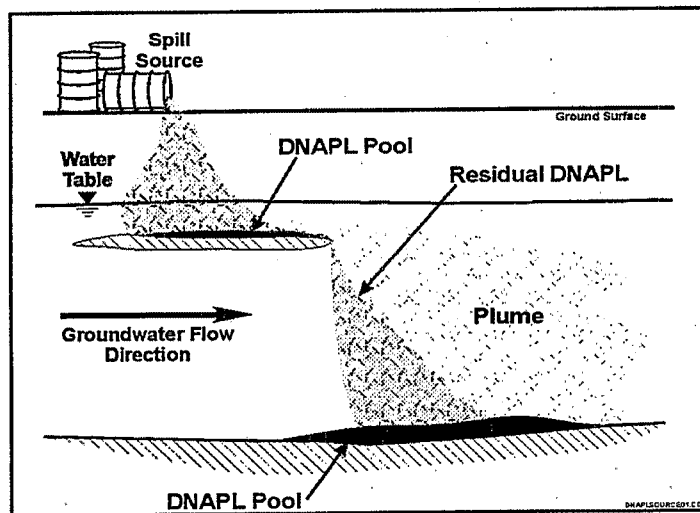
PESCHLA + ROCHMES GMBH
Umwelttechnik - Geotechnik - Hydrogeologie - Datenmanagement

SITE-SPECIFIC VERIFICATION OF IN SITU REMEDIATION OF DNAPLS

Arun Gavaskar¹

Dense nonaqueous-phase liquid (DNAPL) contamination is turning out to be more widespread than first imagined, especially as site owners and their representatives get better at finding DNAPL source zones. DNAPL is most commonly encountered at sites contaminated with chlorinated solvents, such as trichloroethylene (TCE) and perchloroethylene (PCE). These solvents were used in many industrial activities, such as metal finishing, dry cleaning, and maintenance. Past use and disposal practices have led to the appearance of these solvents in the subsurface. Because many of these solvents are denser than water, they often penetrate the water table and continue to migrate downward until they encounter a low-permeability layer. Depending on the nature of its saturation of the soil pores, DNAPL is considered either mobile or residual. Mobile DNAPL can be displaced from the pores that it occupies by a strong hydraulic gradient. Residual DNAPL, on the other hand, cannot be displaced by hydraulic gradient alone, no matter how strong. Therefore, it cannot be pumped out of extraction wells, as in the case of mobile DNAPL.

Figure 1: Illustration of a DNAPL Source Zone Forming.



Many of these solvents are resistant to natural degradation in the solvent phase and are only sparingly soluble in water. In addition, their mass transfer to the dissolved phase is often further retarded by an array of factors, such as complex soil pore geometries. Therefore, even a spill or leak of one drum of solvent can continue to dissolve and contaminate an aquifer for several years or decades. In many aquifers, the dissolved phase or plume generated encounters little retardation (from factors such as adsorption or degradation). Therefore, these plumes can often travel long distances and threaten drinking water sources and other receptors.

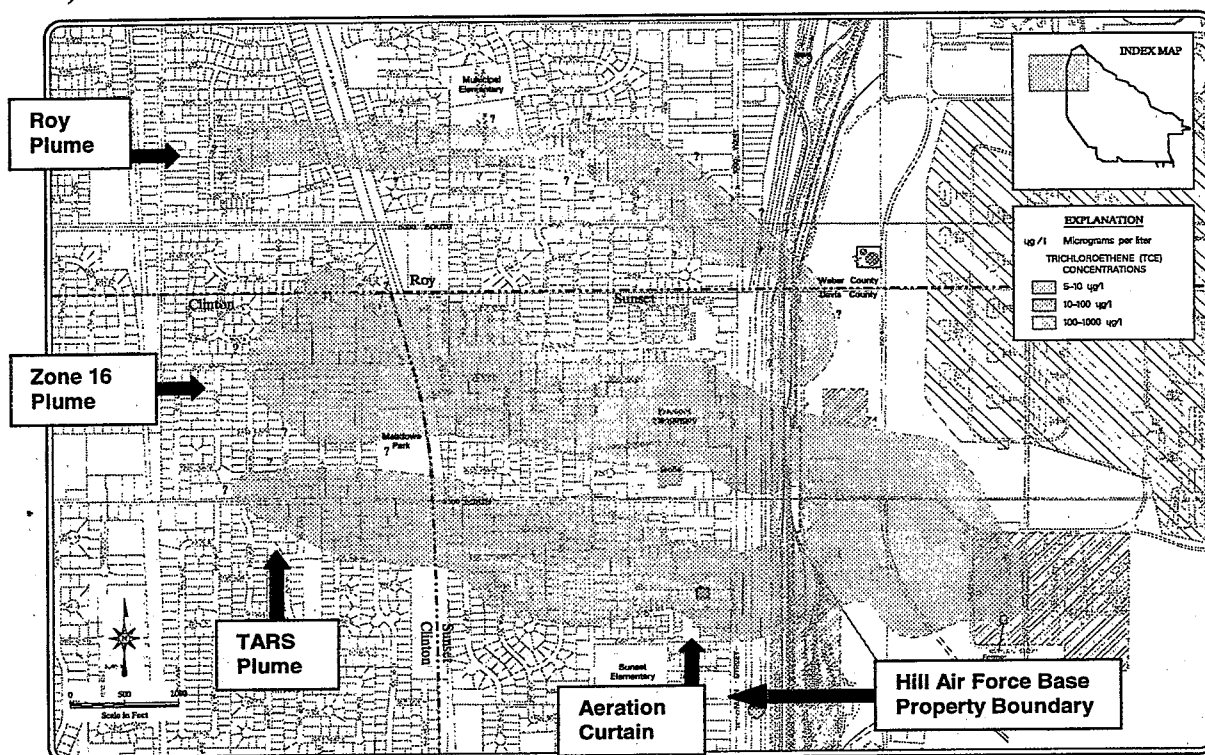
1. CHANGES IN DNAPL SITE CHARACTERIZATION

One challenge in finding DNAPL source zones is that their downward migration is governed by geologic heterogeneities and preferential pathways, rather than the hydraulic gradient. In addition, many sites have suffered spills and leaks in multiple and often unknown locations. This has led to the presence of multiple subsurface sources on a single property, resulting in multiple overlapping plumes. At such sites, DNAPL

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sometimes may occur in counterintuitive locations. At many sites, even those with an apparent plethora of monitoring wells, the monitoring well density may not be enough to distinguish between multiple plumes, let alone multiple sources. For example, at one of the most challenging sites, Operable Unit 5 in Hill Air Force Base, Utah, fairly extensive initial monitoring led to the discovery of what was thought to be only one plume (see Figure 2). Subsequently, additional monitoring led to the identification of three plumes. An expert panel that recently reviewed the abundant monitoring data could not be sure whether the three plumes originated from a single source or multiple sources. Multiple wells and soil borings over approximately one square mile of suspected source area have failed to reveal any definite sources. Whether or not a source, if it is narrowly defined as DNAPL or solvent phase, still exists at this site is not yet clear. If such a source exists, the DNAPL mass is probably relatively small, but diffuse.

Figure 2: TCE Plumes at Operable Unit 5, Hill Air Force Base, Utah (Source: Montgomery Watson, 2001).



2. CHALLENGES IN DNAPL SITE REMEDIATION

There are two schools of thought on how to deal with DNAPL sites; both schools represent thoughtful and valid arguments, indicating that the learning process still continues.

One school of thought argues that most DNAPL source zones are recalcitrant to characterization and treatment. In this school, success is ultimately measured by an improvement in downgradient groundwater quality (reduction in dissolved contaminant concentrations to target cleanup levels at a downgradient compliance boundary, which is often the property boundary). Proponents of this school use three arguments:

- The practical difficulties encountered in finding and delineating DNAPL sources
- The technical and economic limitations in removing 100% of the DNAPL mass at a site

- (c) Modeling simulations, which show that DNAPL mass removal would have to be nearly 100%, before any significant improvement in groundwater quality is encountered at the compliance boundary (Freeze and McWhorter, 1997; Cherry et al., 1996).

The first school argues that at many sites, because of the complex nature of the DNAPL distribution, even the best characterization efforts may fail to completely delineate the source and some parts of the DNAPL source could fall outside the zone targeted for remediation. Therefore, not only is DNAPL remediation limited by the technical and economic limitations posed by the asymptotic nature of DNAPL mass recovery encountered during most remediation applications, but that the intrinsic complexity of the DNAPL distribution at most sites assures an outcome that is less than 100% successful in removing the source. This would lead to the continued presence of a dissolved contaminant plume that the site owner would have to address. A better approach at many sites would be to leave the source alone and focus the remedy on containing the plume.

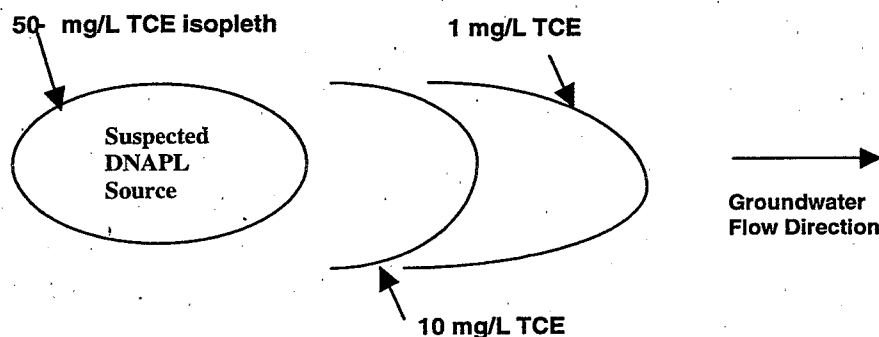
The second school of thought primarily argues that any DNAPL mass removal is welcome. Success need not be defined so absolutely. Site owners are getting better at characterization and at finding and delineating DNAPL source zones. As long as DNAPL source zones are reasonably well defined and remediation technologies are able to remove a reasonable amount (say, 60 to 90%) of DNAPL mass from the affected aquifer, there is a good chance that the resulting plume is weakened to the point where natural attenuation may be sufficient to achieve target cleanup levels at a downgradient compliance boundary. Even if an active remedy, such as a pump-and-treat system, is required to contain a post-source remediation plume, the life of the plume would probably have been greatly reduced by the weakening of the source that feeds it. In addition, this school argues that models showing persisting downgradient plume concentrations, following substantial DNAPL mass removal, are based on homogeneous aquifers. In most aquifers, which are heterogeneous to varying degrees, removal of some DNAPL mass (probably from the more permeable regions of the aquifer, where most remediation technologies are particularly effective) would cause the bulk of the groundwater flow to encounter less DNAPL. Most of the remaining DNAPL would be trapped in pores that are inaccessible to the bulk flow. Therefore, in most cases, downgradient contaminant concentrations should be lower, following substantial DNAPL mass removal.

3. IMPLICATIONS FOR SITE OWNERS

Because both schools of thought present valid arguments backed by theoretical simulations and practical experience, it appears that DNAPL sites will have to be approached on a case-by-case basis. The first school's argument is strengthened by the fact that at many sites, such as former NAS Moffett Field and Dover AFB, passive plume containment remedies, such as natural attenuation or permeable barrier have been found to be effective and economical (Gavaskar et al., 2000; Gavaskar et al., 1998). Even an active remedy, such as a pump-and-treat system, is not as uneconomical as it used to be. With the development of concepts, such as slow pump and treat (Cherry et al., 1996), in which pumping is conducted at the lowest rate necessary to contain a plume, at many sites, it may be possible to contain fairly large plumes with relatively small pump-and-treat operations (1 to 5 gal/min). Previously, more aggressive pump-and-treat operations aimed at treating and removing the plume were much more costly. In addition, at some sites, pump-and-treat systems are already installed as an interim remedy and could be optimized for more effective containment and favorable economics. The development of high capacity and more compact "low-profile" or tray-type air strippers has also contributed to reducing the space and cost requirements of pump-and-treat systems (Battelle and Duke Engineering & Services, 2001). In addition, as seen at Operable Unit 5, Hill Air Force Base, the probability of even finding the DNAPL source may be minimal. However, there are also sites where the technical feasibility and economics may favor source delineation and remediation. For example, at some sites, such as Naval Air Station Pensacola, Florida, the source zone has been more broadly defined as the area inside the isopleth with the highest concentration of the contaminant (see illustration of this type of site in Figure 3). Because this high-dissolved phase concentration area identified was relatively small, source remediation efforts were focused in this *suspected* source area without additional effort to find actual DNAPL phase. Therefore, DNAPL site

characterization and remediation is as much an art as a science; much is left to the collective judgment of site owners and their representatives (scientific consultants and attorneys), regulators, and other stakeholders.

Figure 3: Suspected Source Area Ringed by Highest Identified Groundwater Concentration.



At Launch Complex 34, Cape Canaveral Air Station, Florida, for example, TCE has entered the subsurface in such large quantities that a moderate characterization effort (relative to the size of the site) was able to find and adequately delineate the source. In addition, the large mass of DNAPL, perched on a relatively thin clay aquitard underlying the surficial aquifer, was threatening the confined aquifer below. Although there are signs that over the last 30 to 40 years, some DNAPL has progressed to the confined aquifer in areas where the aquitard is particularly thin, removal of DNAPL mass from the surficial aquifer has greatly reduced the risk to the confined aquifer. Significant contamination of confined aquifers due to DNAPL present in surficial aquifers is a risk that potentially threatens drinking water supplies and increases the potential costs of any future remediation or plume containment efforts.

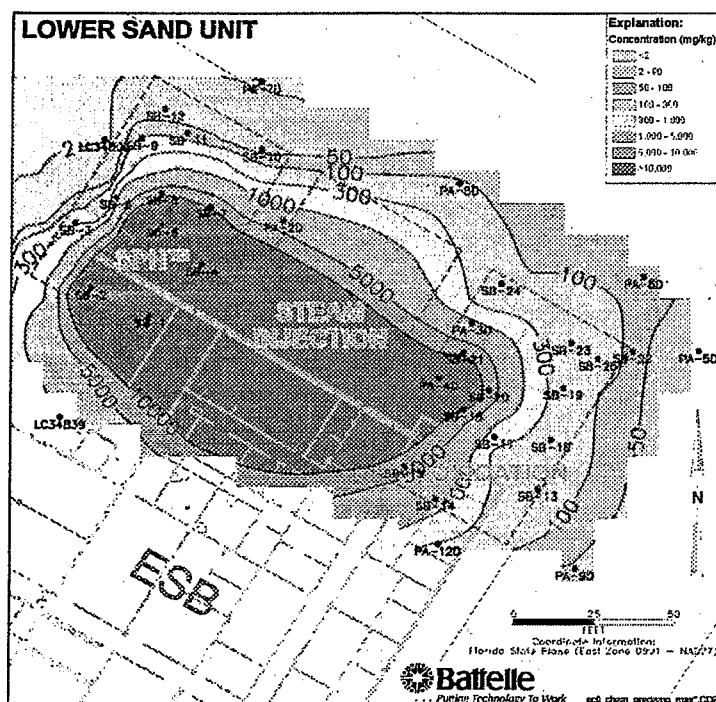
The first school would argue that remediation of the source zone increases the risk of DNAPL migration – downwards or to the sides; this may increase the contamination in the aquitard or the cleaner confined aquifer below or it may lead to a widening of the source, and hence, the plume in the surficial aquifer. Therefore, remediation of the DNAPL in the surficial aquifer would have to be done in a way that minimizes the potential for further downward migration of DNAPL due to the remediation technology application itself. This would seem to favor technologies that promote destruction of the DNAPL in the subsurface, rather than those that promote mobilization and extraction of the DNAPL to the surface for aboveground treatment. Much better hydraulic control would be required for DNAPL mobilization technologies, although engineering controls are necessary for any source remediation effort.

4. CHALLENGES IN DEFINING AND VALIDATING THE SUCCESS OF DNAPL SITE REMEDIATION

DNAPL is a relatively new problem. The widespread nature of this problem was first recognized in the 1990s. Remediation and monitoring approaches for this problem are still evolving. One shortcoming in several DNAPL remediation technology demonstrations has been inadequate monitoring and/or the limitations of the monitoring instruments themselves. Two demonstrations in the U.S. that have attempted more comprehensive monitoring of DNAPL source zones and the effects of the remediation efforts are the Interagency DNAPL Consortium's (IDC) demonstration of three remediation technologies—chemical oxidation, resistive heating, and steam injection – at Cape Canaveral Air Station (Battelle, 2001 a and b) and the Environmental Security Technologies Certification Program's (ESTCP) demonstration of surfactant flushing at Marine Corps Base at Camp Lejeune, North Carolina (Duke Engineering &

Services, 2000). Although different monitoring tools were used in the two demonstrations, considerable effort was made in both demonstrations to track, not just the reduction in groundwater concentrations and any aboveground DNAPL recovery (as is typical in previous remediation efforts), but also the initial mass and fate of the DNAPL in the aquifer.

Figure 4: DNAPL Source Zone (300 mg/kg and higher contours) at Cape Canaveral Air Station Identified through Extensive Soil Sampling.



The apparent success or failure of DNAPL treatment can sometimes be a matter of data collection and interpretation. As an example, Table 1 presents a restricted data set from the resistive heating demonstration at Cape Canaveral Air Station representative of the level of monitoring and data collection conducted at many remediation sites. All the data in Table 1 indicate success at removing DNAPL mass (1,947 kg of TCE recovered aboveground) and improving groundwater quality (as much as 99% decline in groundwater TCE concentrations). Much of the remaining TCE appears to have been degraded by the treatment, as evidenced by the increase in chloride.

On the other hand, Table 2 shows the results of more comprehensive monitoring conducted at the Cape Canaveral site, through characterization and estimation of the pretreatment DNAPL mass, installation and monitoring of depth-discrete perimeter wells, and analysis of the pre- and post-treatment groundwater geochemistry. Extensive soil sampling and kriging (statistical analysis) were used to obtain a range of estimates for the pre-treatment and post-treatment TCE mass, at the 80% confidence level. Spatial coverage of the heterogeneous DNAPL distribution was improved by collecting nearly 300 soil samples during each event from the 75 ft long x 50 ft wide x 45 ft deep test plot in the DNAPL source zone. Methanol extraction procedures for the soil samples were modified to allow extraction of larger aliquots of soil, thus allowing the entire subsurface soil column to be extracted and analyzed at each of 12 locations in the test plot. The main advantage of depth-discrete groundwater and soil sampling over some other tools is that spatial coverage is not dependent on geologic heterogeneities in the aquifer or on specific DNAPL properties. Collecting a sufficiently high number of soil samples, with the number being determined by the expected variability of the TCE distribution and the desired level of statistical confidence, gave the site owner reasonably good estimates of the pre- and post-demonstration TCE

masses. Of course, this degree of characterization and monitoring is not likely to be economically feasible for most full-scale remediation sites. However, in the early stages of development of DNAPL source remediation options, comprehensive monitoring is necessary to identify potential shortcomings of the remediation approach and design improved applications at future sites.

Table 1: Interpretation of DNAPL Remediation by Resistive Heating at Cape Canaveral Air Station with a Basic Monitoring Scheme Typical of Many Remediation Projects.

Monitoring Parameter	Pre-Treatment Level	Post-Treatment Level	Change
TCE in Source Zone Well PA-13I	1,070,000 µg/L	60,200 µg/L	- 94 %
TCE in Source Zone Well PA-14I	960,000 µg/L	174,000 µg/L	- 82%
TCE in Source Zone Well PA-14D	868,000 µg/L	2,730 µg/L	- 99%
TCE Mass Recovered Aboveground in Extracted Vapor	--	1,947 kg	--
Chloride in source zone well PA-13D	774 mg/L	3,610 mg/L	+ 366%
Chloride in source zone well PA-14D	774 mg/L	4,790 mg/L	+ 519%

The more comprehensive data in Table 2 now indicate a strong probability that the DNAPL mass recovered aboveground is a fraction of the DNAPL mass that was initially in the subsurface. Because the TCE mass recovered aboveground does not account for the entire difference between the pre- and post-demonstration TCE masses, it is probable that substantial amounts of TCE either degraded or migrated from the treatment plot. Possible pathways for TCE degradation include enhanced biodegradation (due to the enhanced action of microbes at elevated temperatures) and/or abiotic reduction (due to reaction with cast iron shot used in the heating electrodes). However, chloride, which could have been a key indicator of the degradation pathway, loses some significance due to the fact that the substantial increase in groundwater chloride was accompanied by a similar increase in other dissolved ions, namely, sodium, potassium, calcium, and carbonate (alkalinity), which are all seawater constituents.

Given the closeness of this site to the ocean and the presence of relatively high salinity in the pre-treatment groundwater at the base of the surficial aquifer, the possibility that the treatment somehow enhanced saltwater intrusion into the test plot cannot be ruled out. This leads to the possibility that some DNAPL migrated out of the test plot during the treatment. Possible pathways for migration include heat-induced volatilization to the vadose zone and atmosphere and the sideways spread of the deeper TCE caused by an intermediate silt layer in the otherwise sandy aquifer. Although the resistive heating technology successfully heated even the more difficult parts of the target aquifer, such as the soil immediately above the clay aquitard at 45 ft below ground surface and the portion of the aquifer under a building, more engineering controls will be required at future site to manage the collection of mobilized TCE, especially in difficult geologic settings.

At Cape Canaveral Air Station, the demonstration of chemical (permanganate) oxidation treatment of the DNAPL in a separate test plot was more conclusive. As seen in Table 3, the disappearance of TCE mass from aquifer in the test plot (treated portion of the DNAPL source zone) and the monitored changes in groundwater present a more integrated picture of TCE oxidation as the major pathway of DNAPL mass removal. The significant increase in chloride in the treated aquifer was not accompanied by a consistent increase in sodium, another major seawater constituent. At the same time, alkalinity (carbonate) levels in the groundwater increased, as would be expected when carbon dioxide generation (oxidation of organic species) occurs in the surficial aquifer. Visual evidence of purple discoloration of soil and groundwater in the treatment zone indicated good distribution of the potassium permanganate oxidant. Pre- and post-treatment slug tests did not indicate any changes in hydraulic conductivity of the aquifer following

treatment. Monitoring of deeper wells and soil cores showed no evidence of DNAPL in the confined aquifer below. Levels of some trace metals (chromium, nickel, and thallium) that were present in the industrial grade potassium permanganate injected in the aquifer rose temporarily, but are expected to subside, once the treatment zone re-equilibrates with the groundwater flow.

Table 2: Interpretation of DNAPL Remediation by Resistive Heating at Cape Canaveral Air Station with a More Comprehensive Monitoring Scheme.

Monitoring Parameter	Pre-Treatment Level	Post-Treatment Level	Change
TCE in Source Zone Well PA-13I	1,070,000 µg/L	60,200 µg/L	- 94 %
TCE in Source Zone Well PA-14I	960,000 µg/L	174,000 µg/L	- 82%
TCE in Source Zone Well PA-14D	868,000 µg/L	2,730 µg/L	- 99%
TCE Mass in Aquifer (80% confidence interval)	7,498 to 15,677 kg	1,031 to 1,535 kg	- 80 to 93%
TCE Mass Removed from Aquifer (80% confidence interval)	--	5,963 to 14,646 kg *	--
TCE Mass Recovered Aboveground in Extracted Vapor	--	1,947 kg	--
Chloride in source zone well PA-13D	774 mg/L	3,610 mg/L	+ 366%
Chloride in source zone well PA-14D	774 mg/L	4,790 mg/L	+ 519%
Sodium in Source Zone Well PA-13D	369 mg/L	2,070 mg/L	+ 461%
Sodium in Source Zone Well PA-14D	325 mg/L	3,130 mg/L	+ 863%

* Estimated as the difference between the pre-treatment and post-treatment TCE mass estimates in the aquifer. This TCE mass removed estimate is significantly higher than the TCE mass of 1,947 kg recovered aboveground

Therefore, at least during the continuing developmental phase of in-situ DNAPL remediation technologies, a comprehensive characterization of pre-treatment and post-treatment contaminant mass, aquifer geochemistry and hydrology, and the regions surrounding the treated source zone is desirable to understand the true effectiveness of the treatment. Once these remediation technologies are proven and the level of engineering controls appropriate for each class of technology has been identified, it is anticipated that characterization and monitoring requirements will gradually recede. For a well-engineered treatment system, the primary pre-treatment characterization objective would be identification of the boundaries of the DNAPL source zone and distribution of the hot spots in the zone, not the exact DNAPL mass. This would ensure that the treatment is targeted where it is most needed, and minimize (but not fully eliminate) the potential for unidentified pockets of DNAPL pockets outside the treatment zone. The primary post-treatment monitoring objective would be a reduction in groundwater concentrations of the contaminants to target cleanup levels at the compliance boundary. Long-term monitoring would be required to ascertain that the cleanup levels are sustainable and are not subject to a rebound in groundwater contaminant concentrations, once a new post-treatment equilibrium is established in the aquifer.

If the target (regulation-mandated or risk-based) cleanup level is not achieved or achievable in the long term at the compliance boundary, a secondary treatment would be required. The secondary treatment could take any one of several forms – natural attenuation, pump-and-treat system (albeit for a shorter future period and for a weaker plume), or secondary source treatment (probably, some form of enhanced bioremediation). In this sense, three time-based goals are envisioned for remediation of a DNAPL source zone:

Table 3: Interpretation of DNAPL Remediation by Chemical Oxidation at Cape Canaveral Air Station with a More Comprehensive Monitoring Scheme.

Monitoring Parameter	Pre-Treatment Level	Post-Treatment Level	Change
TCE in Source Zone Well BAT-2S	1,110,000 µg/L	< 5 µg/L	- 99 %
TCE in Source Zone Well BAT-2D	1,160,000 µg/L	220,000 µg/L	- 81%
TCE Mass in Test Plot Aquifer (80% confidence interval)	6,217 to 9,182 kg	1,511 to 2,345 kg ^a	- 62 to - 84%
	Same as above	2,980 to 3,182 kg ^b	- 49 to - 68%
Chloride in source zone well BAT-2S	53 mg/L	126 mg/L	+ 138%
Chloride in source zone well BAT-2D	722 mg/L	5,070 mg/L	+ 602%
Sodium in Source Zone Well BAT-2S	28 mg/L	68 mg/L	+ 143%
Sodium in Source Zone Well BAT-2D	305 mg/L	91 mg/L	- 70%
Alkalinity (carbonate ^c) in Source Zone Well BAT-2S	316	1,500 mg/L	+ 375%
Alkalinity (carbonate ^c) in Source Zone Well BAT-2D	208	1,300 mg/L	+ 525%

^a TCE mass based on soil sampling conducted immediately following end of oxidant injection treatment.

^b TCE mass based on soil sampling conducted nine months after the end of oxidant injection treatment. The differences between the TCE mass change estimated at the two time points are indicative of sampling variability.

^c Carbonate buildup is indicative of carbon dioxide production through oxidation of organic species.

- A *short-term goal*, which targets maximum achievable DNAPL mass removal. This goal is generally determined by economic considerations and represents an end point for the primary treatment when the short-term cost of achieving incremental DNAPL mass removal becomes excessive. Achievement of this goal can be verified through the use of groundwater and soil sampling or other tools, as well as analysis of any side-streams recovered aboveground.
- An *intermediate-term goal*, which targets achievement of desired cleanup levels at the compliance boundary. It may take a year or several years for flow to re-equilibrate and for extraneous factors (such as diffusion of sequestered contaminants from downgradient fine-grained aquifer media) to subside, before the site owner can even make a determination that the target cleanup level has been achieved at the compliance boundary. It should be noted that the same is the case when source or plume containment, rather than source remediation, is the selected option at a site. For example, in Figure 2, an aeration trench has been implemented near the property boundary as a permeable barrier inside the TARS plume, for the last two years. Although this treatment is effective in terms of the quality of the treated water emerging from the interceptor trench, the downgradient portion of the TARS plume in Figure 2 shows no sign of receding or detaching from the upgradient plume or source. This persistence of downgradient contamination is probably because of the abundance of silty clay lenses, from which contaminants continue to diffuse slowly over time, thus re-contaminating the treated water. Similar persistence of downgradient contamination for several years following effective containment of the plume at the treatment point has been noted at former NAS Moffett Field (Gavaskar, et al. 1998), a site which has a somewhat similar composition of sand channels and clay deposits. Therefore, irrespective of the approach, be it source remediation or plume containment, at many sites, achievement (or non-achievement) of the intermediate goal, which is generally the most important goal that site owners and regulators are interested in, may not be apparent for a year or several years after implementation of the selected remedy.

- The *long-term goal* of any remediation ultimately would be achievement of regulatory cleanup levels or maximum contaminant levels (MCLs) in the source zone and plume, which would indicate that long-term monitoring and/or plume control measures can be dismantled.

The process seems formidable, but as each goal is reached, the costs of managing a site probably decline. The decision making process involved in selecting the appropriate remedy or chain of remedies and for selecting the tools for characterization and monitoring is driven by a mix of technical, regulatory, and economic factors that is determined on a site-specific basis.

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6. ACKNOWLEDGEMENTS

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7. PRESENTATION VISUALS ~ presented by Arun Gavaskar

Site-Specific Validation of In-Situ Remediation of DNAPL

Presented at NATO Special Session
September 11, 2001

By
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Dense Non-Aqueous Phase Liquid (DNAPL)

- Residual (trapped) DNAPL and Mobile (can flow under strong hydraulic gradient) DNAPL

Location of Aboveground Spill (Primary Source) ↓



Low
Permeability
Layers

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Site Categories with Significant DNAPL

- Chlorinated solvent sites (e.g. perchloroethylene [PCE], trichloroethylene [TCE])
 - Drycleaners
 - Maintenance (Aircraft, ships, automotive)
 - Metal finishing (vapor degreasing)
 - Electronics manufacturing
 - Fire training areas
- Wood treaters (polycyclic aromatic hydrocarbons [PAHs])
- Manufactured Gas Plant (MGP) sites

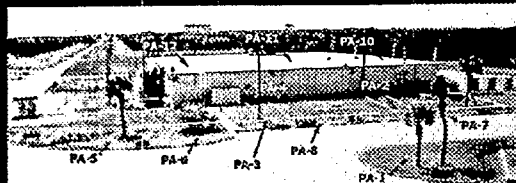
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DNAPL Site Strategies

- What are the Remediation Options Available?

- Source Identification and Remediation (growing interest)
 - Excavation/ Soil Vapor Extraction
 - Heating (Resistive or Steam)
 - Chemical Oxidation (Permanganate or Fenton's reagent)
 - Surfactant flushing
- Source/Plume Containment (most commonly done)
 - Natural attenuation
 - Pump and treat (slow)
 - Permeable barriers (e.g., zerovalent iron, air sparging, biological)
- Plume Treatment (becoming rare)
 - Pump and treat (aggressive)
 - Enhanced bioremediation or bioaugmentation
- Secondary Treatment of DNAPL (becoming an issue)
 - Treating the residuals left behind by primary treatment

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DNAPL Remediation at Cape Canaveral Air Station
- Interagency DNAPL Consortium

- DNAPL source characterization and in-situ treatment (75 ft x 50 ft test plots)
 - Six-Phase Heating
 - Chemical Oxidation
 - Steam Injection

Performance Strategy and Goals

- Cape Canaveral Air Station

- Overall goal - Meet Florida State-mandated maximum contaminant level (MCL) targets in DNAPL Source Area: 3 ug/L TCE, 70 ug/L DCE, and 1 ug/L vinyl chloride
- Goal for Remediation Vendors - Remove 90% of initial DNAPL mass
- Performance Assessment Methodology
 - Primarily, detailed soil sampling
 - Secondly, detailed groundwater and air emissions sampling to verify fate of chlorinated volatile organic compounds (CVOCs)
 - Are CVOCs being destroyed?
 - Is DNAPL migrating to surrounding regions?
 - Are all the CVOCs removed from the test plot being captured aboveground?

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Finding and Characterizing DNAPL Source at Cape Canaveral
- Site Characterization/ Performance Assessment Tools

- Outdoor and indoor characterization may be required
 - DNAPL is often under buildings
- Continuous soil cores from ground surface to aquitard (45 ft bgs) collected and extracted in the field
- 12 soil coring locations x 23 two-foot samples per location in each test plot (entire two-foot length of each sample was extracted)

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Performance Strategy and Goals

- Technical Impracticability Waiver Guidance

- "...Sources should be located and treated or removed where feasible and where significant risk reduction will result, regardless of whether EPA has determined that groundwater restoration is technically impracticable..."
[in other words, a DNAPL source should be located and treated as efficiently as possible, even though any remaining DNAPL may prevent the remediation from achieving MCLs (e.g., 5 ug/L of TCE). Inability to remove 100% of the source should not stop sites from attempting DNAPL source treatment]

Directive 9234.2-25

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Monitored Natural Attenuation Policy

- "...EPA expects that MNA will be most appropriate when used in conjunction with other remediation measures (e.g., source control, groundwater extraction), or as a follow up to active remediation measures that have already been implemented..."

Directive 9200.4-17P

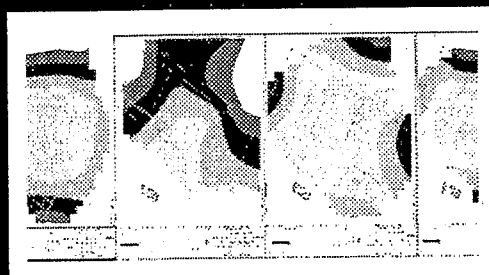
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Del Amo Record of Decision (ROD) Excerpt
- Benefits of DNAPL Source Treatment

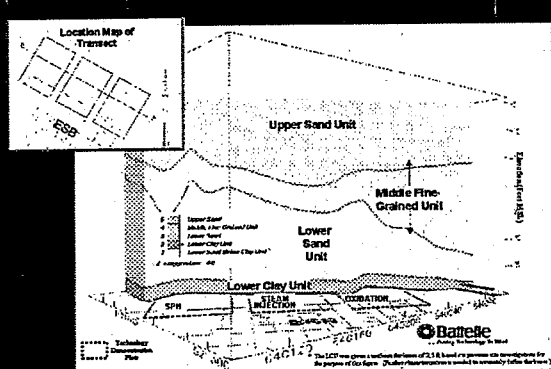
- "...When NAPL is recovered from the ground, its mass and saturation are reduced. In principle, this can (1) reduce the amount of time that the containment zone must be maintained, (2) reduce the potential for NAPL to move naturally either vertically or laterally, and (3) increase the long-term certainty that the remedial action will be protective of human health and remain effective..."

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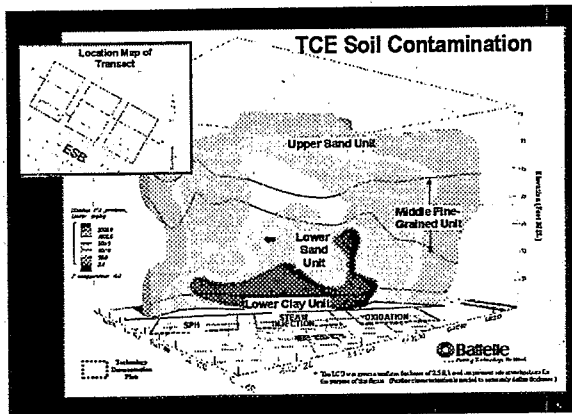
Cape Canaveral Air Station: TCE Distribution in Groundwater at Different Depths (multilevel wells/ well clusters provide first indication of DNAPL Source)



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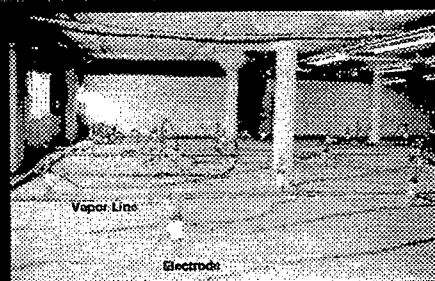


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Industrial Site in USA

- Six-Phase Heating Under a Building



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Cape Canaveral Remediation - Validation of Performance
- Contouring (Linear Interpolation) and Kriging Mass Estimates in Chemical Oxidation Plot

Method	Pretreatment Mass (kg)		Post-treatment Mass (kg)		Removal	
	Avg.	80% Confidence Interval	Avg.	80% Confidence Interval	Avg.	80% Confidence Interval
Contouring Total TCE	6,122		1,333		82 %	
Contouring - DNAPL	5,039		810		84 %	
Kriging Total TCE	7,393	6,347 - 8,122	1,823	1,344 - 2,345	75 %	62 - 84 %

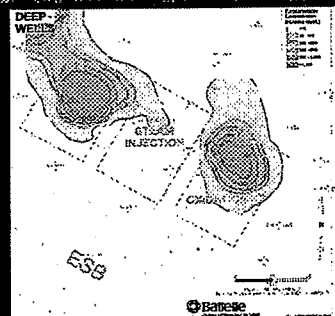
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Cape Canaveral Remediation - Validation of Performance
- Using Inorganic Aquifer Constituents for Validation

Plot of Chloride in Excess of Background Concentrations in the Deeper Wells at Cape Canaveral

• Attributed to oxidation of TCE in Chemical Oxidation Plot

• Difficult to determine source of chloride in SPH Plot (could be TCE degradation or saltwater intrusion)



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Cape Canaveral Remediation - Validation of Performance

- Using Perimeter Monitoring Wells, Surface Emission Tests, and Hydraulic Measurements to Evaluate Potential for TCE/DNAPL Migration



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- Monitoring wells on perimeter of treatment area used to monitor for sharp increases in CVOs that would indicate TCE/DNAPL migration
- As confining layer is relatively thin, monitoring wells were required in the confined aquifer below
- Surface emission testing is desirable, especially for thermal (e.g., steam injection) or exothermic technologies (e.g., Fenton's reagent)
- Water level measurements and slug tests used to determine unusual changes in hydraulic behavior of the aquifer before, during, and after the remediation

DNAPL Source Treatment - Economics

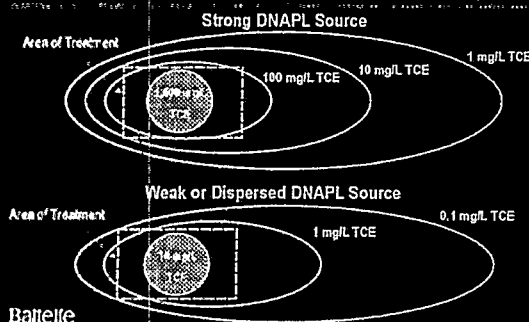
- Present Value (PV) Analysis of Chemical Oxidation versus Pump-and-Treat at Cape Canaveral

- Total cost of chemical oxidation (three injection events) in 75 ft x 50 ft x 40 ft test plot = \$850,000
 - Assumed that natural attenuation is sufficient to control a weakened plume
 - If further source control or plume control is required, total cost will be higher
- Present value of equivalent pump-and-treat system (2 gpm) for containment of DNAPL source for the next 30 years = \$1,032,000
 - Includes capital investment of \$102,000
 - Includes routine annual O&M cost of \$44,000 (2.9% discount rate)
 - Periodic equipment replacement costs
- Monetary advantage of source treatment is not immediately obvious from PV analysis
 - Risk reduction and earlier (long-term) dismantling of plume control measures are the main benefits

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What if we cannot find the source, or the source is likely to be relatively small or weak?

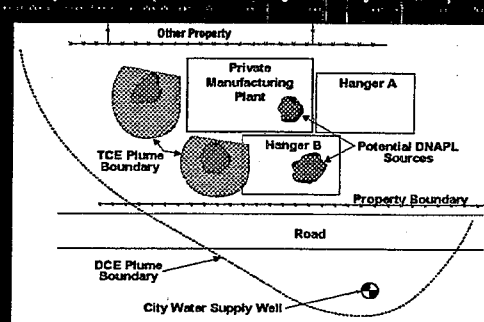
- Treatment of hot spots or plume control may be better remedy



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Private Manufacturing Facility, Eastern USA

- Few dispersed TCE spots detected, large DCE/Vinyl chloride plume



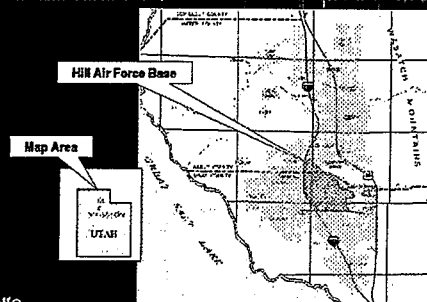
Private Manufacturing Site Strategy

- Selectively characterize hot spots and uncharacterized areas under the buildings
- Determine why TCE is biodegrading to DCE and VC, but DCE and VC continue to persist
- Make a judgment on whether it would be more economical to treat (biologically or otherwise) TCE hot spots or contain/treat DCE plume
- Get agreement from EPA on suitable end point/closure strategy
- Apply the selected remedy

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What if the source is weak, widely dispersed, and probably uneconomical to treat?

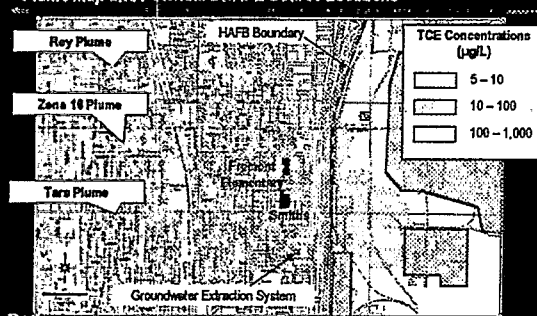
- Hill Air Force Base: Site Location Map



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Hill Air Force Base, Operable Unit 5

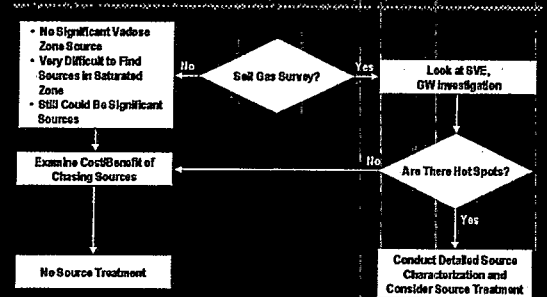
- Plume Map and Potential DNAPL Source Locations



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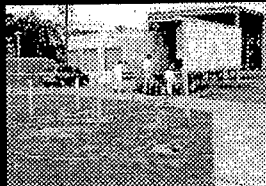
Hill Air Force Base - Operable Unit 5

- Performance Strategy and Goals proposed by Expert Panel



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What if DNAPL Source Remediation Removes only a Part of the Source? - The need for secondary treatment of DNAPL source

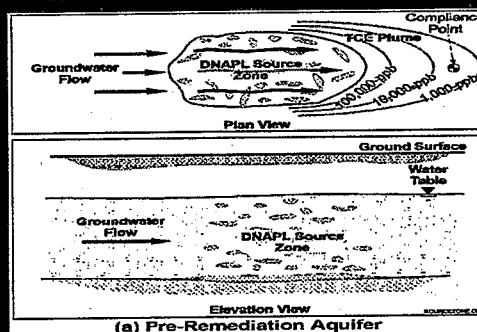


Most primary remediation technologies (e.g., oxidation, heating, or surfactant) are likely to remove 60 to 95% of initial DNAPL source mass

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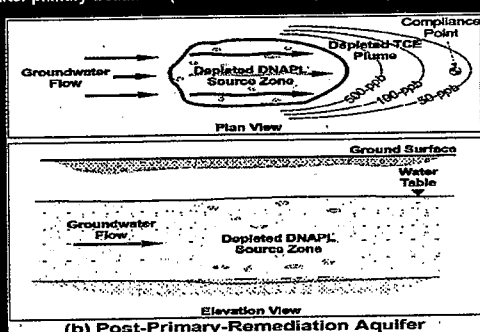
- Naval Air Station Pensacola, Florida: 30 ft x 80 ft source
- Confining clay layer 40 ft bgs
- Initial TCE = 3,000 ppb in source area
- Primary treatment: Fenton's Reagent Oxidation
- Post-Fenton's Treatment, TCE level = nondetect
- Rebound: Six months after treatment, TCE = 100 ppb
- Rebound: One year after treatment = 500 ppb
- Rebound: 1.5 years after treatment = 500 ppb

DNAPL Source Zone – Before Remediation



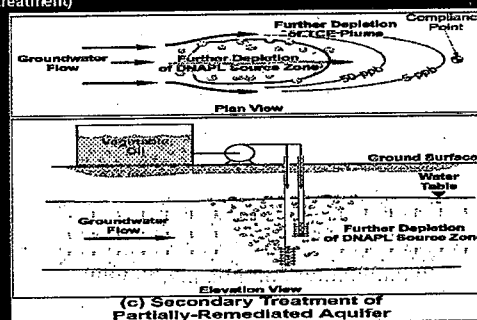
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After primary treatment (chemical oxidation, steam injection, etc.)



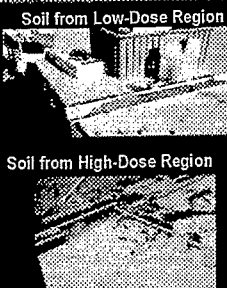
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Secondary Treatment with vegetable oil (planned at Naval Air Station Pensacola, where chemical oxidation was primary treatment)



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Viability of Secondary (Long-Term) Treatment of DNAPL Source



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- Primary remediation is never uniform – some regions receive higher dose of treatment agent (e.g., permanganate or heat) than other regions
- Can microbial populations survive in the low-dose and/or high-dose regions?
- Can these surviving populations be stimulated to enhance degradation of contaminants?

Microbes survive harsh treatment. Addition of a carbon source can stimulate microbial growth in both low-dose and high-dose regions of DNAPL Source

Treatment Type/ Region	Heterotrophic Counts (CFU/mL) ^(a)			
	T=0		T= 5 Months	
High Temp.	Aerobic 4.6×10^7	Anaerobic 2.9×10^7	Aerobic 3.3×10^5	Anaerobic 1.7×10^7
Low Temp.	Aerobic 2.7×10^7	Anaerobic 8.7×10^5	Aerobic 4.3×10^5	Anaerobic 3.9×10^5
High KMnO ₄	Aerobic $<1.0 \times 10^1$	Anaerobic $<1.0 \times 10^1$	Aerobic 1.9×10^5	Anaerobic 9.4×10^5
Low KMnO ₄	Aerobic 1.0×10^1	Anaerobic 7.4×10^1	Aerobic 1.9×10^5	Anaerobic 7.0×10^5
Killed Control	Aerobic $<1.0 \times 10^1$	Anaerobic $<1.0 \times 10^1$	Aerobic $<1.0 \times 10^1$	Anaerobic $<1.0 \times 10^1$

Secondary Treatment of DNAPL Source

- Approximate Cost of Carbon Sources

Source: Harkness, M. in *Bioremediation and Phytoremediation of Chlorinated and Recalcitrant Compounds*, Battelle Press, 2000.

Carbon Source	Cost (\$/lb of carbon)
Lactate	1.0 to 2.2
Ethanol	0.20 to 0.25
Vegetable Oil	0.20 to 0.50
HRC™ (poly-acetate)	12.00
Methanol	0.04 to 0.05

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Strategy for Chlorinated Solvent Sites, Part 1 - For Long-Term Economical Remediation

- Conduct selective additional site characterization to determine if an active source or DNAPL can be identified
 - Soil gas survey
 - Depth-discrete monitoring points or wells
- If source can be identified and can be economically treated, focus on source treatment (e.g., oxidant injection)
 - Short-Term Goal: Remove as much DNAPL as economical
 - Intermediate Term Goal: Secondary treatment (e.g. carbon source or some plume control (e.g., natural attenuation or pump-and-treat)
 - Long-Term Goal: Earliest possible dismantling of plume control system possible

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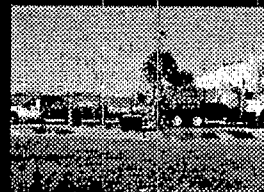
Strategy for Chlorinated Solvent Sites, Part 2**- For Long-Term Economical Remediation**

- If source cannot be identified or is too disperse or is too uneconomical to treat, then focus on plume control
 - Try and obtain a TI waiver for on-property contamination
 - Evaluate aquifer characteristics for risk assessment and determine the feasibility of natural attenuation
 - Determine if hotspots can be treated with enhanced bioremediation (addition of carbon source) or by bioaugmentation (introducing suitable microbes)
 - If plume is a threat to potential receptors, treat plume at property boundary
 - Evaluate permeable barriers or pump & treat systems or other active remedy

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**Site-Specific Validation of
In-Situ Remediation of DNAPL**

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FUTURE DEVELOPMENTS IN VERIFICATION OF IN SITU PERFORMANCE: EXPECTATIONS, INSTRUMENTS, AND GOALS

Bert Satijn¹

1. KEY ISSUES OF TECHNICAL PRESENTATIONS

The second day of the NATO/CCMS special session is dedicated to the technical issues of in situ technologies and validation aspects. This last presentation reviews technical contributions and picking up the key issues. These will be used as a base for a presentation of future developments in the field of performance testing and validation processes.

1.1 Soil Vapor Extraction- Michael Altenbockum

In Germany a large-scale review of executed soil vapor extraction projects has been executed. It became clear that in many cases the project team was not very well aware of the processes in subsoil. The overall conclusion of the reviewer was "They don't know what they are doing". Performance testing and validation was not done properly due to lack of experience and knowledge of the actual geochemical phenomena in the soil.

Energy consumption seemed to be a good parameter for cost efficiency. Energy is not only the important factor for the costs, but in relation with the total quantity of removed contaminants, it provides a good indication for the removal efficiency and environmental efficiency of the whole operation.

Conclusions of the study were, that Quality Assurance as integral part of the project needs more emphasis. The preparation of adequate guidelines in a kind of handbook or checklist could be an important aid to improve the performance of soil vapor extraction systems. In Germany they are working on these guidelines.

Validation should not only after the project being an issue. Especially during operation validation tools can provide the necessary information to modify the system and to adapt operation.

1.2. Surfactant/Cosolvent Flushing- Leland Vane

Validation of the performance of surfactant and cosolvent flushing is complicated, due to the complicated processes in subsoil. Although in many cases used, it is clear that groundwater monitoring is not the only and right validation tool. Concentrations in groundwater do not show the overall impact of the desorbing or mobilizing effect of the adsorbed contaminants on soil particles. No information will be gathered from the fate of the contaminants still (partly) adsorbed on the soil particles. It only provides evidence of the mass, diluted in the groundwater. To get more information of the residual bound contaminants on soil particles other methods are needed. Partitioning interwell tracer tests, PITT, are one of the promising new techniques. In fact with this technique the fate of the contaminants in the subsoil is "photographed", by injecting a tracer into the hot spot and recovering it down stream. The recovery curve in the monitoring wells provides information on mass and location of NAPLs. PITT is fitting as characterization and validation tool.

But it is clear that to do a good validation a combination of different validation tools is required to provide evidence, that performance of the remediation system is adequate.

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1.3 Validation of In Situ Bioremediation by Applying Isotopes- Frank Volkering

Before validation of in situ bioremediation it is required to consider the parameters and criteria used. Next to the traditional parameters (concentrations in soil and groundwater, mass removal, etc.), last year's new lines of evidence have been developed, like hydrogen concentrations, DNA/RNA and isotopes.

Microorganisms do prefer to start with the lighter isotopes before cracking the heavier ones, as has been proven in many laboratories in batch tests. This phenomenon is called *fractionating of stable isotopes*. In one of the SKB-projects at the industrial site of DOW Chemicals in the Netherlands this method has been used successfully to validate the anaerobic degradation of benzene. It is expected that the application of analysis of stable isotopes will provide in future more possibilities for validation of the complex subsoil processes.

1.4 In Situ Chemical Oxidation- Robert Siegrist

In situ chemical oxidation is a new emerging technology for the elimination of hot spots. Also for this technique performance tests and validation tools are badly needed. Given the complex processes dealing with multiple evidence is needed for validation. Each method is providing us some part of the subsoil puzzle. One can think of a combination plume load measurements, mass destruction balances, bioassays and surface geophysics.

Compared to the traditional methods, it seems to be necessary to provide more evidence to prove that the new remediation system will be successful. But how much certainty do we have to give?

1.5 In Situ Permeable Reactive Barriers- Volker Birke

In Germany there are several experiences with reactive barriers. Reactive barriers are techniques on the boundary of in situ and ex situ. Validation of the performance is therefore a little bit easier than in case of the real in situ techniques. Installation of monitoring wells upstream, in the wall and downstream will provide the information on process conditions, efficiency and side effects. The technology is focused on an efficient removal of contaminants in the barrier without too much difficulty during exploitation. In many cases the barrier is designed to accommodate geochemical processes, for example the iron walls to eliminate the Tri and Per. But the anomaly in the subsoil is promoting biochemical processes, which easily creates clogging. The performance of active barriers might therefore be endangered due to bacterial growth in the barrier material or at the interface between soil and barrier.

In Germany the RUBIN network is established to develop and exchange knowledge on active barriers.

1.6 In Situ Remediation of DNAPLS- Arun Gavaskar

DNAPLs are made *not* to be discovered and *not* to be removed. This is the conclusion after studying so many projects on remediation of DNAPLs. The traditional approach of Pump and Treat is seldom successful. Pump & Treat becomes Pump & Spill due to the ever-lasting emissions from the source area. But the efficiency of source removal is sometimes disappointing. In sandy soils with new contaminants and retraceable source, there are possibilities of a removal rate of 90%. But in other cases it reaches up to 60 or 70%. So secondary treatment is normally necessary. It is also useful to realize that mobilizing the source and partial removing it, creates a situation in which the residue is normally more mobile than before. Without secondary treatment emissions to the plume will be bigger than before during a certain period after shaking up the source. The design of treatment system has to be based on a combination of primary and secondary treatment.

2. DEVELOPMENTS OF IN SITU TREATMENT

In situ remediation is a young science, only ten years old. The challenge of heterogeneity and complex biogeochemical processes makes the "remediator" a "geoartist". Site-specific circumstances influence the performance of techniques heavily. More understanding of processes by proper evaluation and research is needed. Better combinations of ex situ and in situ might provide solutions. Source boosting and plume management will be in many cases the right approach: better combinations of different in situ techniques with the right energy at the right time and place.

The consultants do not have enough knowledge and experience to propose such combinations. The contractors are normally specialized in one technique and are unable or unwilling to offer the right combination. This has also to do with the hardware; each technique requires its own system of hardware. But in future hardware has to be developed in such a way that the same equipment could be used for the subsequent phases in remediation.

The secondary treatment after partial removal of the source, is taking normally a long period. Therefore integration of clean up and redevelopment of the location could be thought over.

3. INSTRUMENTS AND GOALS FOR VALIDATION

Validation of in situ processes is based on the understanding of these processes. The available equipment is not sophisticated enough to provide the wanted evidence in many cases. More sophisticated monitoring tools are to be developed in the future, like cone penetration tests with specific probes for all relevant parameters to register the processes. Cheaper tools are needed in order to be able to get better spatial and time depending information.

Further development of sensors and effect related monitoring (bioassays) is important. But also the link to legislation should not be forgotten. Legislation is mainly based on concentrations, although risk based guidelines are becoming more and more important.

All these wishes do require quite some research funds. The economic developments and the political attention for soil quality is as such, that more money for these purposes is not to be expected. Therefore it is recommended to strengthen the international exchange of knowledge and data. An international performance database with information on the performance (well documented) of in situ techniques and methods to validate the performance could contribute to further development despite the recent developments in world society.

Although it will remain a challenge to be successful as "geoartists", the improvement of in situ techniques, hand in hand with its validation tools, has to contribute to a more predictable and cost efficient performance in soil quality management.

4. PRESENTATION VISUALS ~ presented by Bert Satijn

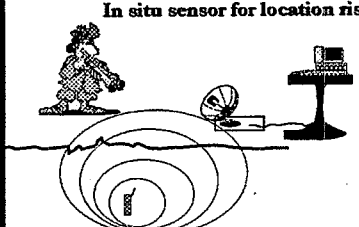
Future developments in validation
of in situ performance, expectations,
instruments & goals

Bert Satijn
SKB, Dutch Foundation for
knowledge development and transfer on soil
quality management

NATO/CCMS Special Session
Liege, 10 and 11 September 2001

10-09-01 NATO/CCMS special session

Solium 3:
In situ sensor for location risk validation



Monitoring tool for the future

10-09-01 NATO/CCMS special session

Outline of Presentation

- Recommendations of today's presentations
- Developments of in situ treatment
- Instruments and goals for validation
- Plenary discussion of field experiences and future developments

10-09-01 NATO/CCMS special session

Key issues of presentations

- Soil vapor extraction Michael Altenboeckum
 - ~ "They don't know what they are doing"
 - ~ Energy consumption as parameter for cost efficiency
 - ~ Quality assurance and guidelines are important
 - ~ Validation not only afterwards but especially during operation
- Surfactant/cosolvent flushing Leland Vane
 - ~ Groundwater monitoring is not the right validation tool
 - ~ PPT is fitting for characterization and validation tool
 - ~ Combination of different validation tools is necessary

10-09-01 NATO/CCMS special session

Key issues of presentations (2)

- In situ bioremediation Frank Volkering
 - ~ Criteria for validation
 - ~ New lines of evidence: hydrogen, DNA/RNA and isotopes
 - ~ Fractionating of stable isotopes
 - ~ In future more possibilities
- In situ chemical oxidation Robert Siegrist
 - ~ Emerging technology
 - ~ Multiple evidence is needed for validation
 - ~ Pure test, test duration, secondary surface monitoring
 - ~ How much certainty do we have to prove?

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Key issues of presentations(3)

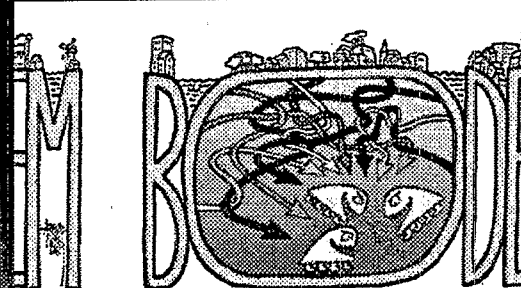
- In situ permeable reactive barriers Volker Birke
 - ~ Reactive barriers are techniques on the boundary of of in situ and ex situ
 - ~ Validation in barriers is more easy
 - ~ Mixed processes in the wall might create clogging
- In situ remediation of DNAPLs Arun Gavaskar
 - ~ DNAPLs are *impossible* to be discovered and *impossible* to be removed
 - ~ Source removal reaches 60-70%
 - ~ Secondary treatment is necessary

10-09-01 NATO/CCMS special session

Developments of in situ treatment

- More understanding of processes by proper evaluation and research
- Better combinations of ex situ and in situ
 - ~ source boosting and plume management
- Better combinations of different in situ techniques
 - ~ the right energy at the right time and place
- Integration of clean up and redevelopment

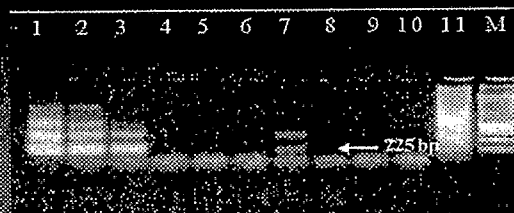
10-09-01 NATO/CCMS special session



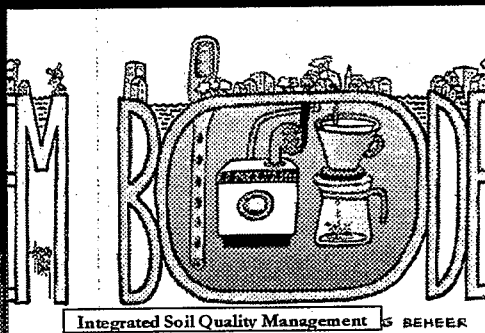
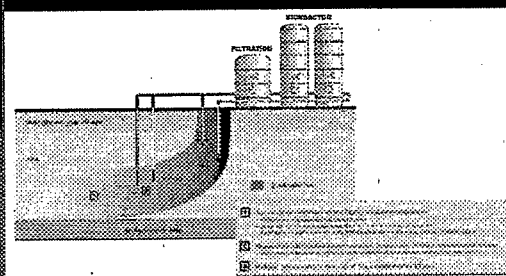
Fundamental and applied research in biodegradation EN

10-09-01 NATO/CCMS special session

Research on biodegradation



Combination of source boosting and plume management

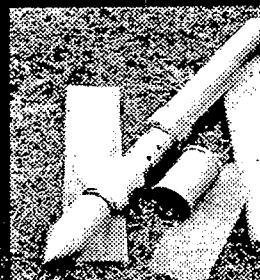


Developments of in situ treatment (2)

- More realistic goals by authorities and *geo-artists*
- Better understanding of risk reduction related to cost efficiency
- Better balance for uncertainties
- Function related risk criteria fitted on location scale (Solium 3)

Instruments and goals for validation

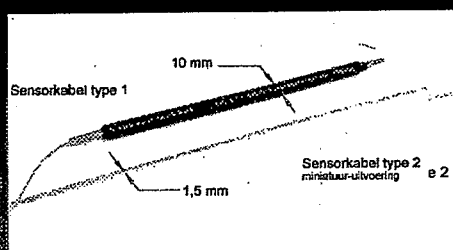
- More sophisticated monitoring tools
 - Cone penetration test with specific probes
 - * more parameters
 - * cheaper
 - * 3D information
 - Further development of sensors and effect related monitoring (bioassays) including link to legislation
- International Performance Database



Cone penetration tests:

- * geotechnical data
- * water sampling
- * pH, temperature, Redox profile
- * camera
- * colour filter

Fiber optic cables



Instruments and goals for validation (2)

- Validation is an integral part of in situ technology
- Validation protocol is determined during planning phase
- Protocol is not denying heterogeneity

Concluding Remarks

- Policy development
- Technology of in situ treatment
- Monitoring devices
- Validation strategies

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PILOT STUDY MISSION

PHASE III C Continuation of NATO/CCMS Pilot Study: Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater

1. BACKGROUND TO PROPOSED STUDY

The problems of contamination resulting from inappropriate handling of wastes, including accidental releases, are faced to some extent by all countries. The need for cost-effective technologies to apply to these problems has resulted in the application of new/innovative technologies and/or new applications of existing technologies. In many countries, there is increasingly a need to justify specific projects and explain their broad benefits given the priorities for limited environmental budgets. Thus, the environmental merit and associated cost-effectiveness of the proposed solution will be important in the technology selection decision.

Building a knowledge base so that innovative and emerging technologies are identified is the impetus for the NATO/CCMS Pilot Study on "Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater." Under this current study, new technologies being developed, demonstrated, and evaluated in the field are discussed. This allows each of the participating countries to have access to an inventory of applications of individual technologies, which allows each country to target scarce internal resources at unmet needs for technology development. The technologies include biological, chemical, physical, containment, solidification/stabilization, and thermal technologies for both soil and groundwater. This current pilot study draws from an extremely broad representation and the follow up would work to expand this.

The current study has examined over fifty environmental projects. There were nine fellowships awarded to the study. A team of pilot study country representatives and fellows is currently preparing an extensive report of the pilot study activities. Numerous presentations and publications reported about the pilot study activities over the five-year period. In addition to participation from NATO countries, NACC and other European and Asian-Pacific countries participated. This diverse group promoted an excellent atmosphere for technology exchange. An extension of the pilot study will provide a platform for continued discussions in this environmentally challenging arena.

2. PURPOSE AND OBJECTIVES

The United States proposes a follow-up (Phase III) study to the existing NATO/CCMS study titled "Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater." The focus of Phase III would be the technical approaches for addressing the treatment of contaminated land and groundwater. This phase would draw on the information presented under the prior studies and the expertise of the participants from all countries. The output would be summary documents addressing cleanup problems and the array of currently available and newly emerging technical solutions. The Phase III study would be technologically orientated and would continue to address technologies. Issues of sustainability, environmental merit, and cost-effectiveness would be enthusiastically addressed. Principles of sustainability address the use of our natural resources. Site remediation addresses the management of our land and water resources. Sustainable development addresses the re-use of contaminated land instead of the utilization of new land. This appeals to a wide range of interests because it combines economic development and environmental protection into a single system. The objectives of the study are to critically evaluate technologies, promote the appropriate use of technologies, use information technology systems to disseminate the products, and to foster innovative thinking in the area of contaminated land. International technology verification is another issue that will enable technology users to be assured of minimal technology performance. This is another important issue concerning use of innovative technologies. This Phase III study would have the following goals:

- a) In-depth discussions about specific types of contaminated land problems (successes and failures) and the suggested technical solutions from each country's perspective,
- b) Examination of selection criteria for treatment and cleanup technologies for individual projects,
- c) Expand mechanisms and channels for technology information transfer, such as the NATO/CCMS Environmental Clearinghouse System,
- d) Examination/identification of innovative technologies, and
- e) Examining the sustainable use of remedial technologies looking at the broad environmental significance of the project, thus the environmental merit and appropriateness of the individual project.

3. ESTIMATED DURATION

Meetings: November 1997 to May 2002

Completion of final report: June 2003

4. SCOPE OF WORK

First, the Phase III study would enable participating countries to continue to present and exchange technical information on demonstrated technologies for the cleanup of contaminated land and groundwater. During the Phase II study, these technical information exchanges benefited both the countries themselves and technology developers from various countries. This technology information exchange and assistance to technology developers would therefore continue. Emphasis would be on making the pilot study information available. Use of existing environmental data systems such as the NATO/CCMS Environmental Clearinghouse System will be pursued. The study would also pursue the development of linkages to other international initiatives on contaminated land remediation.

As in the Phase II study, projects would be presented for consideration and, if accepted by other countries, they would be discussed at the meetings and later documented. Currently, various countries support development of hazardous waste treatment/cleanup technologies by governmental assistance and private funds. This part of the study would report on and exchange information of ongoing work in the development of new technologies in this area. As with the current study, projects would be presented for consideration and if accepted, fully discussed at the meetings. Individual countries can bring experts to report on projects that they are conducting. A final report would be prepared on each project or category of projects (such as thermal, biological, containment, etc.) and compiled as the final study report.

Third, the Phase III study would identify specific contaminated land problems and examine these problems in depth. The pilot study members would put forth specific problems, which would be addressed in depth by the pilot study members at the meetings. Thus, a country could present a specific problem such as contamination at an electronics manufacturing facility, agricultural production, organic chemical facility, manufactured gas plant, etc. Solutions and technology selection criteria to address these problems would be developed based on the collaboration of international experts. These discussions would be extremely beneficial for the newly industrializing countries facing cleanup issues related to privatization as well as developing countries. Discussions should also focus on the implementation of incorrect solutions for specific projects. The documentation of these failures and the technical understanding of why the project failed will be beneficial for those with similar problems. Sustainability, environmental merit, and cost-benefit aspects would equally be addressed.

Finally, specific area themes for each meeting could be developed. These topics could be addressed in one-day workshops as part of the CCMS meeting. These topic areas would be selected and developed by the pilot study participants prior to the meetings. These areas would be excellent venues for expert speakers and would encourage excellent interchange of ideas.

5. NON-NATO PARTICIPATION

It is proposed that non-NATO countries be invited to participate or be observers at this NATO/CCMS Pilot Study. Proposed countries may be Brazil, Japan, and those from Central and Eastern Europe. It is proposed that the non-NATO countries (Austria, Australia, Sweden, Switzerland, New Zealand, Hungary, Slovenia, Russian Federation, etc.) participating in Phase II be extended for participation in Phase III of the pilot study. Continued involvement of Cooperation Partner countries will be pursued.

6. REQUEST FOR PILOT STUDY ESTABLISHMENT

It is requested of the Committee on the Challenges of Modern Society that they approve the establishment of the Phase III Continuation of the Pilot Study on the Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater.

Pilot Country: United States of America
Lead Organization: U.S. Environmental Protection Agency

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Participating Countries: Australia, Austria, Belgium, Canada, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Ireland, Japan, New Zealand, Norway, Poland, Portugal, Slovenia, Sweden, Switzerland, The Netherlands, Turkey, United Kingdom, United States

Scheduled Meetings: February 23-27, 1998, in Vienna, Austria
May 9-14, 1999, in Angers, France
June 26-30, 2000, in Wiesbaden, Germany
September 9-14, 2001, in Liège, Belgium
May 5-10, 2002, Rome, Italy

